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U. S. Navy  
Office of Naval Research  
Research Contract N7onr-529  
Task Order II  
Project 158-070

CHEMICAL THERMODYNAMICS OF MATERIALS AT HIGH TEMPERATURES

Technical Report No. 14

SOLID SOLUTION EQUILIBRIA IN THE TITANIUM SYSTEM  
ZIRCONIUM - OXYGEN - HYDROGEN

by

R. K. Edwards, P. Levesque and D. Cabiocchetti

August 1955

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By R. K. Edwards, P. Levesque,<sup>1,2</sup> and D. Cubicciotti<sup>3</sup>

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- (1) Based on part of a thesis submitted by Pascal Levesque to the Graduate School of Illinois Institute of Technology in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1953.
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ABSTRACT

The solubility of hydrogen in the solid solution of the ternary system zirconium-oxygen-hydrogen has been determined as a function of temperature, composition, and equilibrium hydrogen pressure. The data have been correlated with those of the related binary systems and some previous work in the ternary system, and the solid state chemistry has been represented by an extensive provisional partial ternary phase diagram.

A new single-phase region,  $\delta$ , lying between the  $\alpha$ -zirconium and  $\epsilon$  (approximately  $ZrH_2$ ) phases has been established as belonging both in the binary and ternary systems.

The hydrogen saturation boundary of the  $\alpha$ -phase shows that initially hydrogen may be replaced by oxygen on a three-to-one basis in the  $\alpha$ -phase. The hydrogen saturation boundary of the  $\delta$ -phase indicates that hydrogen may be replaced by oxygen on a three-and-one-half to one basis in the  $\delta$ -phase.

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INTRODUCTION

The solid solubility of oxygen in zirconium metal has long been considered to be very high.<sup>4,5</sup> A recent thorough phase diagram study in

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- (4) J. H. de Boer and J. D. Fast, Z. anorg. Chem., 148, 345 (1925).
  - (5) D. Cubicciotti, J. Am. Chem. Soc., 73, 2032 (1951).
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the zirconium-oxygen system by Domagala and McPherson<sup>6</sup> has set the solubility

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- (6) R. F. Domagala and D. J. McPherson, "Phase Diagrams of Zirconium-Base Binary Alloys, Report No. 10, The Zirconium-Oxygen System, Report 4 - Summary COO-181," Armour Research Foundation, Chicago, Illinois, March 31, 1953.
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at 29 atom per cent oxygen in the temperature range 600 to 900°. We have previously presented a partial phase diagram for the zirconium-hydrogen system and have indicated a primary solid solubility for hydrogen in zirconium of from 49 atom per cent at 700° to 52 atom per cent at 875°. <sup>7</sup> Hall, Martin,

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- (7) R. K. Edwards, P. Levesque, and D. Cubicciotti, "Solid Solution Equilibria in the Zirconium-Hydrogen System," Tech. Report No. 13, U. S. Navy, Office of Naval Research, Contract N7-ONR-329, Task Order II, August (1953).
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- (8) (Mrs.) M. N. A. Hall, S. L. H. Martin, and A. L. G. Rees, Trans. Faraday Soc., 41, 306 (1945).
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zirconium-oxygen solid solutions, observed that apparently the "volume of hydrogen sorbed at saturation decreased by a volume equivalent to that of oxygen present." This observation has been considered of notable interest by Smith,<sup>9</sup> who presumably was concerned with the implications of such

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- (9) D. P. Smith, "Hydrogen in Metals," The University of Chicago Press, Chicago, 1948.
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behavior with regard to his "rift theory" as the mode of occlusion of hydrogen in metals.

It occurred to us that the observed "equivalence" might be nothing more than a manifestation of the conversion of  $ZrH_2$  to  $ZrO_2$  on addition of oxygen since these are the "saturation" phases with respect to the two components, hydrogen and oxygen. On the other hand the wide solid solubility, discussed above, of both hydrogen and oxygen in zirconium would lead to a prediction of extensive ternary solubility. One might envisage this ternary solution as a metallic zirconium matrix lattice with the interstices variously filled

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with the small hydrogen and oxygen particles. The idealized hexagonal close-packed lattice can provide both octahedral and tetrahedral interstices. We might expect some rather striking manifestations as oxygen replaces hydrogen in view of their conspicuous differences in size and in electron affinities. We have previously mentioned<sup>7</sup> the work of Coehn and coworkers which showed hydrogen in palladium solid solution to migrate with passage of an electrical current as though it were a positively charged particle. In contrast, de Boer and Fast<sup>4</sup> and Alnutt and Scheer<sup>10</sup> have

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- (10) D. B. Alnutt and C. L. Scheer, Trans. Electrochem. Soc., 88, 195, (1945).
- 

shown that oxygen in zirconium migrates as a negatively charged particle.

The present investigation was conducted by the method of measuring the equilibrium hydrogen pressure over ternary solid solutions as a function of composition and temperature. The composition was varied by successive additions of measured volumes of hydrogen to an initially homogeneous zirconium-oxygen solid solution in which the composition ratio of zirconium to oxygen remained constant.

#### EXPERIMENTAL

Each zirconium-oxygen solid solution specimen was prepared by controlled oxidation of about 100 mg. of 0.015-inch diameter zirconium wire, followed by equilibration of the resulting metal and oxide mixture for twenty minutes in vacuum at a temperature approximately 200° below the melting point of the particular composition. Equilibration heating was by electrical resistance of the wire in vacuum. The apparatus is shown in Figure 1, and the procedure has been previously described.<sup>5</sup> The homogeneous nature of each preparation was carefully established by x-ray diffraction examination before it was considered a suitable specimen for study. After the composition was established by weight difference on oxygen uptake as observed on an Ainsworth semi-micro balance, a middle section of the wire was cut out for use in the hydrogen solubility determination.

Numerous preliminary attempts at equilibration by holding a preparation at 1200° for twelve hours did not always result in a homogeneous single phase solution, and the procedure was abandoned as unreliable. Hall, Martin, and Rees reported the latter procedure to be satisfactory at 950° in their work.<sup>8</sup>

## MATERIALS

Zirconium wire of 0.015-inch diameter obtained from the Foote Mineral Company was used. The analysis has been given previously.<sup>7</sup> Commercial 99.8 per cent pure tank oxygen was used without additional purification.

## PROCEDURE

The apparatus and procedure for determining the equilibrium hydrogen pressure as a function of temperature and composition of the ternary material were those we had used in the binary zirconium-hydrogen study, and the same limits of error are assumed.<sup>7</sup> Families of isotherms were determined for samples of initial oxygen compositions of 6.3, 10.8, 18.6, 24.7, and 29.6 atom per cent in zirconium, and these values correspond to atom ratios,  $R$ , of oxygen to zirconium of 0.068, 0.121, 0.229, 0.328, and 0.420, respectively.

## RESULTS

The experimental pressure-composition isotherms are shown on two different coordinate bases. Figures 2, 3, 4, 5, and 6 show families of isotherms of equilibrium hydrogen pressure as a function of the volume of hydrogen gas taken up per gram of zirconium metal in a sample of given  $R$  value. Figures 7, 8, 9, 10, and 11 show corresponding plots of the logarithm of the hydrogen pressure versus the logarithm of the atom per cent hydrogen composition. Advantage was taken of the reasonably linear nature of the extrapolations in the logarithmic plots to obtain the phase field boundary compositions plotted in Figures 12, 13, 14, 15, and 16, and listed in Table 1. In Figures 2 and 3, one sees the unmistakable appearance of a second composition region of pressure arrest in addition to the one corresponding to the arrest in the binary system.<sup>7</sup> The data shown on the 800° isotherm in Figure 2 are the results of four different determinations and amply establish the existence of the second arrest.

On the other hand, Figures 4, 5, and 6 show only wide composition ranges of a single pressure arrest. Values of equilibrium hydrogen pressure as a function of temperature at several significant fixed compositions have been taken from the smoothed curves of Figures 2, 3, 4, 5, and 6 and the data are tabulated in Table 2 and plotted in Figures 17, 18, 19, 20, and 21 with the logarithm of the equilibrium hydrogen pressure as a function of the reciprocal temperature. From the plots partial molal heats of solution



of molecular hydrogen in the ternary solid solutions were obtained, and these values are also given in Table 2.

A summarizing correlation is given in Figure 22 where an isothermal section of a provisional ternary phase diagram is shown in part. The data for the binary zirconium-hydrogen system boundaries were taken from our previous paper.<sup>7</sup> The data for the binary zirconium-oxygen system boundaries were taken from Domagala and McPherson.<sup>6</sup> The data of the composition region of R value greater than 0.420 we have obtained from replotting the data of the isotherms of Hall, Martin, and Rees,<sup>8</sup> in the manner of the handling of our own data.

### DISCUSSION

The solid state chemistry of the zirconium-oxygen-hydrogen system in the temperature range 600 to 900° and at hydrogen pressures of less than 760 mm. of Hg can be shown by a quasi-ternary phase diagram of  $\text{Zr} - \text{ZrO}_2 - \text{ZrH}_2$  as is presented in Figure 22. It is to be borne in mind that actually somewhat less than the hydrogen composition corresponding to  $\text{ZrH}_2$  is reached under the given temperature and pressure conditions.<sup>7</sup> Nomenclature of phase fields is that previously adopted.<sup>7</sup>

A three-component system in the presence always of a gas phase will yield invariant isothermal pressure behavior with changing composition if three solid phases are present. In the following discussion the presence of a gas phase is to be understood and only the solid phases are explicitly discussed. The two-phase regions, however, may appear to show equivalent behavior if the change in composition happens to be effected along a tie-line connecting phase compositions of equal fugacity. As compositions are continuously and isothermally changed along a path traversing first a single phase, second a two-phase, and third a three-phase region, one would expect the following general behavior. The pressure isotherm would change continuously in the one-phase region and also in the two-phase region, with a change in slope at the join of these regions, and it would finally change in slope at the boundary and remain invariant throughout the three-phase region.

An interesting consequence of the natural phase relations and the manner in which composition changes were effected in the present study is that for each material of a given R value, pressure-composition isotherms clearly indicate that the composition traverses were essentially along

tie-lines in the two-phase regions. That this is not three-phase behavior can be seen by noting that pressures do actually vary in the regions indicated in Figure 22 to be two-phase regions. A three-dimensional plot having the isothermal ternary diagram as a base and hydrogen fugacity as the vertical ordinate would readily demonstrate this point. We have indicated the observed behavior in the ternary diagram by showing the two-phase regions shaded with lines presumed to closely approximate lines of constant fugacity. Induction of the nature of the phase diagram was based on the above, and on the additional requirements that adjoining single-phase regions must be separated by a two-phase field and adjoining two-phase fields must be separated by a three-phase field. Room temperature x-ray diffraction patterns were taken on all of the fully hydrogenated specimens and in all cases the  $\Sigma$ -phase<sup>7</sup> accounted for all diffraction lines. In particular, and somewhat to our surprise at first, none of the  $\text{ZrO}_2$  diffraction pattern was found for any of these specimens. The diagram given is consistent with this observation.

A preparation of  $R = 0.121$ , of such a hydrogen composition as to place it just inside the  $\delta$ -region on the zirconium-rich side, was examined by x-ray diffraction at room temperature. The relative intensities and positions of the lines of the pattern, except for one line, could be reasonably well correlated with patterns of  $\alpha$ -zirconium, assuming appreciable distortion of the lattice. However, the one additional line of medium to strong intensity and low Bragg angle was unmistakably present. The broadness of the lines, like that generally found<sup>8</sup> in the patterns taken on materials in the binary zirconium-hydrogen system, precluded more detailed structural analysis.

The partial molal heats of solution of molecular hydrogen in the ternary solid solutions are found to be the same as in the binary zirconium-hydrogen system<sup>7</sup> for the  $\alpha$  phase and  $(\alpha + \delta)$  two-phase fields for the materials of  $R$  values 0.068 and 0.121. For the latter, the  $(\delta + \Sigma)$  two-phase field yielded  $\bar{\Delta H} = -29.7$  Kcal per mole as did the  $\alpha$  phase and  $(\alpha + \Sigma)$  two-phase fields for all higher  $R$  values. It is to be added that the significance of the  $\bar{\Delta H}$  values for the two-phase regions may be questioned since their composition boundaries are not constant, as is discussed briefly below.

The temperature dependence of the various phase field boundaries may be seen in Figures 12, 13, 14, 15, and 16. One may note a tendency toward closure of the  $(\alpha + \delta)$  and  $(\delta + \Sigma)$  fields at higher temperatures.

We have not discussed the presence of the  $\beta$ -phase region in this ternary study since from the known binary zirconium-oxygen system behavior<sup>6</sup> it is most probable that the region would have been displaced to temperatures higher than those used in this study.

One may refer to the x-ray diffraction patterns by Sidhu and McGuire<sup>11</sup>

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(11) S. S. Sidhu and J. C. McGuire, J. App. Phys., 23, 1257 (1952).

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for an idea of the magnitude and nature of the changes in the diffraction pattern as hydrogen is added to hafnium metal.<sup>12</sup>

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(12) The quality of the patterns obtained with hafnium is considerably superior to that obtained with zirconium.

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We urge a reasonable caution in the use of the diagram we present and wish to note in particular the uncertainty in the actual apex positions of the three-phase fields. The extent of the uncertainty may be easily inferred on noting the amount and nature of the extrapolation of boundaries to these apex positions. The extrapolation to the ( $\delta + \epsilon$ ) two-phase field boundaries leads to boundary compositions of about 61 and 62 atom per cent hydrogen for the binary zirconium-hydrogen system. We suppose that the value 62 atom per cent given for the hydrogen-rich boundary is probably quite accurate since the linear extrapolation nicely parallels the isothermal composition isobars, one of which is shown for the pressure 760 mm. of Hg by the dotted line in the  $\epsilon$ -region of Figure 22. On the other hand, a strictly linear extrapolation of the data for the zirconium-rich ( $\delta + \epsilon$ ) border would have led to a composition only negligibly lower than 62 atom per cent so that it may well imply an extremely narrow corresponding region in the binary zirconium-hydrogen system. Furthermore, if the boundary were taken as linear through the data points plotted, it would imply the relationship that the hydrogen saturation limit of the  $\delta$ -phase decreases in a manner which shows oxygen to replace hydrogen on a three-and-one-half to one atom basis. The rather extensive linear portion of the hydrogen-rich  $\alpha$ -phase saturation boundary, similarly considered, implies that oxygen will replace hydrogen on a three-to-one atom basis.

In the  $\alpha$ -zirconium hexagonal close-packed structure, one would suppose that the oxygen atoms would fill the octahedral interstices—the largest holes available. Apparently they cannot do so completely or the solubility limit of oxygen in zirconium in the binary zirconium-oxygen system would correspond to 50 atom per cent. The actual limit of 29 atom per cent shows that about two out of every five available octahedral interstices in  $\alpha$ -zirconium become filled at saturation with oxygen.

On the other hand, hydrogen may be either in tetrahedral interstices or in the octahedral interstices. If it is in the latter, the hydrogen binary saturation composition of 50 atom per cent in the zirconium-hydrogen system would indicate that all available octahedral interstices are filled. It appears then that each oxygen atom which enters the lattice denies more of the interstitial sites to hydrogen than it does to oxygen itself. This would seem to indicate a form of repulsion through general lattice strain and to rule out any special stabilization one might have anticipated to arise from proximate metallic hydrogen. Effects due to the difference in electron affinities between oxygen and hydrogen seem to be absent.

The dotted line in Figure 22 represents the contour of an isothermal composition isobar for a hydrogen pressure of 760 mm. of Hg and is therefore our value of the "saturation" composition as the term was used by Hall, Martin, and Rees.<sup>8</sup> It is seen that oxygen does replace hydrogen on approximately a one-to-one basis as supposed, but that this point is of trivial interest since "saturation" in that sense represents no phase field limit.

Table 1 Boundary Compositions of Solid Two-Phase Fields in the  
Zirconium-Oxygen-Hydrogen System  
 (Compositions in Atom % Hydrogen)

R		TEMPERATURES →				
		600°	700°	750°	800°	850°
0.068	(two two-phase regions) First	—	—	42.8	42.9	45.7
		—	50.1	51.2	51.2	53.7
	Second	—	56.6	56.2	55.6	—
		—	58.0	58.0	58.0	—
0.121	(two two-phase regions) First	—	34.8	35.9	36.7	39.1
		—	42.7	43.4	44.2	47.0
	Second	51.9	51.9	51.8	51.5	—
		55.6	55.3	55.0	54.3	—
0.229	(single two-phase field)	—	25.7	25.3	25.0	—
		49.0	48.4	49.6	49.6	—
0.328	(single two-phase field)	—	15.0	17.1	17.1	—
		45.2	45.7	46.8	47.3	—
0.420	(single two-phase field)	—	9.6	12.0	12.0	—
		38.9	38.9	38.9	39.3	—

Table 2 Equilibrium Hydrogen Pressure as a Function of Composition in the  
Ternary Zirconium-Oxygen-Hydrogen System  
(Pressures in mm. of Hg.)

R	Phase Region	Hydrogen Composition Atom %	$\Delta \bar{H}$ of Solution Kcal./mole	TEMPERATURES					
				600°	700°	750°	800°	850°	900°
0.068	$\alpha$	31.4	-39.6	—	—	10	27	60	125
	$\alpha$	37.9	-39.6	—	9	24	65	145	270
	$\alpha + \delta$	47.8	-49.6	—	15	55	165	480	—
	$\delta + \epsilon$	57.2	—	15	140	290	472	—	—
	$\epsilon$	60.4	—	100	450	660	—	—	—
0.121	$\alpha$	30.4	-39.6	—	—	18	48	100	212
	$\alpha + \delta$	42.1	-49.6	—	13	45	150	455	—
	$\delta$	48.6	—	6	53	150	342	605	—
	$\delta + \epsilon$	53.8	-29.7	43	165	310	595	—	—
	$\epsilon$	58.0	—	280	560	775	—	—	—
0.229	$\alpha$	11.7	-29.7	—	20	40	80	145	250
	$\alpha$	16.6	-29.7	—	46	95	200	325	510
	$\alpha + \epsilon$	39.8	-29.7	35	135	300	515	—	—
	$\epsilon$	53.0	—	285	485	648	—	—	—
	$\alpha$	5.8	-29.7	—	12	24	49	85	155
0.328	$\alpha$	10.9	-29.7	10	35	70	160	290	440
	$\alpha + \epsilon$	35.5	-29.7	30	110	275	465	—	—
	$\epsilon$	49.5	—	205	440	650	—	—	—
	$\alpha$	7.9	-29.7	13	50	100	220	375	—
	$\alpha + \epsilon$	25.6	-29.7	25	95	202	390	—	—
0.420	$\epsilon$	42.7	—	110	285	450	660	—	—

Table 3 Equilibrium Hydrogen Pressure as a Function of  
Composition and Temperature  
 (Experimental data for the oxygen-zirconium atom ratio,  $R = 0.068$ )

Pressure mm.Hg	Atom % Hydrogen	Pressure mm.Hg	Atom % Hydrogen	Pressure mm.Hg	Atom % Hydrogen
<u>Run 165-600°</u>		<u>Run 166-750°</u>		<u>Run 157-850°</u>	
0	38.7	177	54.3	22	20.0
12	55.0	257	56.1	53	30.4
60	60.2	<u>Run 158-800°</u>		102	36.2
136	60.6	49	55.8	167	38.9
255	61.0	123	41.3	198	39.5
407	61.9	164	48.1	232	40.6
592	62.5	201	51.5	312	42.6
726	62.8	<u>Run 161-800°</u>		376	43.8
<u>Run 160-700°</u>		14	23.4	443	45.0
14	43.5	93	40.0	473	47.2
20	51.1	147	42.6	502	54.2
89	55.5	289	53.6	586	54.9
142	57.0	714	59.3	720	56.4
288	59.4	<u>Run 163-800°</u>		<u>Run 159-850°</u>	
<u>Run 170-700°</u>		241	52.4	679	55.5
14	43.3	378	54.5	<u>Run 169-850°</u>	
49	53.8	618	58.6	108	35.5
145	58.1	724	59.3	205	39.6
167	58.3	<u>Run 167-800°</u>		310	42.3
277	59.4	38	33.6	<u>Run 159-900°</u>	
383	60.2	119	41.1	26	17.2
517	60.6	190	51.9	63	25.2
624	61.6	360	54.8	123	31.0
731	62.0	405	55.6	184	34.9
<u>Run 164-750°</u>		460	56.2	253	37.3
9	27.3	474	58.2	317	40.0
27	38.0	<u>Run 168-800°</u>		396	42.0
48	41.6	135	41.2	521	44.6
76	52.1	303	53.9	627	45.6
126	53.7	415	55.3	734	46.6
196	55.0	439	55.8	<u>Run 169-900°</u>	
316	58.0	460	56.1	324	39.2
474	59.5	478	57.5	417	42.3
476	59.1	500	58.0	523	43.7
578	60.1	560	58.6	629	45.2
712	60.8	649	59.2		

**Table 4** Equilibrium Hydrogen Pressure as a Function of  
Composition and Temperature

(Experimental data for the oxygen-zirconium atom ratio, R = 0.121)

Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen
<u>Run 201-800°</u>		<u>Run 203-750°</u>		<u>Run 198-850°</u>	
1	39.0	12	25.1	21	16.8
9	50.4	30	32.6	50	23.4
35	53.0	45	40.8	151	32.1
45	56.6	64	45.4	257	34.4
87	57.1	122	47.9	<u>Run 199-850°</u>	
275	58.0	197	49.3	16	15.4
477	58.9	287	51.3	105	30.2
615	59.3	311	53.5	336	36.9
740	59.9	348	55.5	391	38.2
<u>Run 200-700°</u>		488	56.7	440	39.1
5	25.7	603	57.0	462	45.5
13	37.5	743	57.5	498	46.2
21	43.5	<u>Run 197-800°</u>		541	47.9
44	47.3	10	16.0	614	49.0
95	50.2	38	27.8	725	49.8
146	51.2	66	30.9	<u>Run 202-900°</u>	
175	54.5	96	34.3	24	11.4
220	56.0	133	35.8	78	21.8
332	57.0	154	41.0	132	26.8
521	57.8	179	44.6	230	30.9
598	58.1	195	45.8	332	33.4
743	58.9	245	46.9	457	36.1
		314	48.0	638	37.9
		360	48.7	741	38.6
		409	49.6		
		431	50.0		
		492	50.5		
		542	51.3		
		598	53.3		
		662	55.3		
		716	55.5		
		751	55.6		



Table 5 Equilibrium Hydrogen Pressure as a Function of  
Composition and Temperature  
 (Experimental data for the oxygen-zirconium atom ratio,  $R = 0.229$ )

Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen
<u>Run 179-600°</u>		<u>Run 175-750°</u>		<u>Run 172-850°</u>		<u>Run 173-800°</u>	
17	29.8	132	18.7	25	7.2	38	9.8
32	43.4	275	23.2	60	9.9	97	12.7
46	50.3	305	38.9	112	11.6	157	14.4
80	51.9	321	45.5	201	13.6	210	15.8
146	52.6	353	49.0	274	14.5	280	19.0
263	52.5	411	51.2	341	16.4	333	19.2
425	53.7	488	52.4	410	18.0	412	22.8
566	54.2	570	52.5	464	19.8	462	24.8
586	54.4	690	53.2	516	20.2	515	26.4
741	55.1			565	20.1		
<u>Run 179-700°</u>		<u>Run 176-750°</u>		<u>Run 171-900°</u>		<u>Run 174-800°</u>	
599	53.6	50	12.4	623	21.2	50	10.2
<u>Run 180-700°</u>		108	15.4	749	23.2	107	13.1
29	14.7	166	18.0	<u>Run 171-900°</u>		155	14.0
57	19.8	248	22.2	48	4.9	214	16.0
81	23.8	<u>Run 177-750°</u>		114	8.3	270	18.3
117	28.1	20	10.1	194	10.1	305	19.0
131	42.6	41	12.5	301	12.3	372	21.2
164	48.2	67	14.2	410	15.6	437	24.7
220	50.9	106	16.8	543	17.5	506	25.2
327	51.8	152	18.9	656	17.9	<u>Run 178-800°</u>	
458	52.9	202	21.7	752	18.7	438	23.0
600	53.4	258	22.6			505	26.7
727	54.1					505	41.2
<u>Run 181-700°</u>						535	48.6
48	18.0					576	50.1
67	21.1					638	51.3
85	23.9					731	51.9
118	28.3						
135	40.3						

Table 6 Equilibrium Hydrogen Pressure as a Function of  
Composition and Temperature  
 (Experimental data for the oxygen-zirconium atom ratio,  $R = 0.329$ )

Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg.	Atom % Hydro- gen
<u>Run 186-690°</u>		<u>Run 183-750°</u>		<u>Run 188-850°</u>	
12	24.0	24	7.1	73	5.6
21	33.6	61	10.0	175	7.1
26	42.9	100	12.0	255	9.2
42	46.9	154	13.7	352	11.6
<u>Run 186A-600°</u>		204	15.6	464	14.8
25	37.6	255	16.4	554	16.4
45	46.2	277	28.7	619	18.4
77	47.9	289	38.6	727	20.1
137	48.9	<u>Run 184-750°</u>		<u>Run 189-900°</u>	
203	49.4	97	11.4	37	3.7
310	50.2	197	15.2	71	4.1
445	50.9	284	46.0	176	6.2
617	51.8	405	48.4	278	7.3
725	52.4	<u>Run 185A-750°</u>		378	9.3
<u>Run 189-700°</u>		570	49.1	483	13.3
37	10.2	650	49.6	569	13.9
61	13.5	737	50.0	655	14.7
89	18.2	<u>Run 184A-800°</u>		752	16.2
107	35.1	509	47.5		
128	43.0	605	47.8		
184	47.2	733	48.7		
251	48.1	<u>Run 185-800°</u>			
373	49.1	29	5.4		
526	49.9	62	8.5		
685	50.5	137	10.2		
		199	11.0		
		300	12.9		
		400	16.1		
		441	18.2		
		454	32.4		
		474	41.9		
		723	48.3		

Table 7 Equilibrium Hydrogen Pressure as a Function of  
Composition and Temperature  
 (Experimental data for the oxygen-zirconium atom ratio, R = 0.420)

Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen	Pressure mm.Hg	Atom % Hydro- gen
<u>Run 193-600°</u>		<u>Run 193A-750°</u>		<u>Run 194-800°</u>	
18	15.2	57	6.4	35	4.9
30	36.8	130	8.7	148	5.9
53	41.4	<u>Run 195-750°</u>		268	8.3
117	43.0	21	6.0	379	12.5
223	44.1	62	6.8	389	28.1
396	46.0	153	9.3	442	38.9
577	46.8	193	17.0	532	41.5
751	47.5	205	34.0	641	42.7
<u>Run 192-700°</u>		258	40.0	739	43.7
32	6.8	390	41.8	<u>Run 190-850°</u>	
75	10.7	497	43.0	26	2.9
211	41.2	604	43.7	99	4.1
337	43.5	733	44.8	196	5.1
493	44.8	<u>Run 191-800°</u>		324	6.6
599	45.5	29	4.1	478	9.4
750	46.6	89	5.2	585	10.7
<u>Run 196-700°</u>		190	6.9	739	13.9
41	7.4	308	8.6		
94	31.7				
135	39.6				

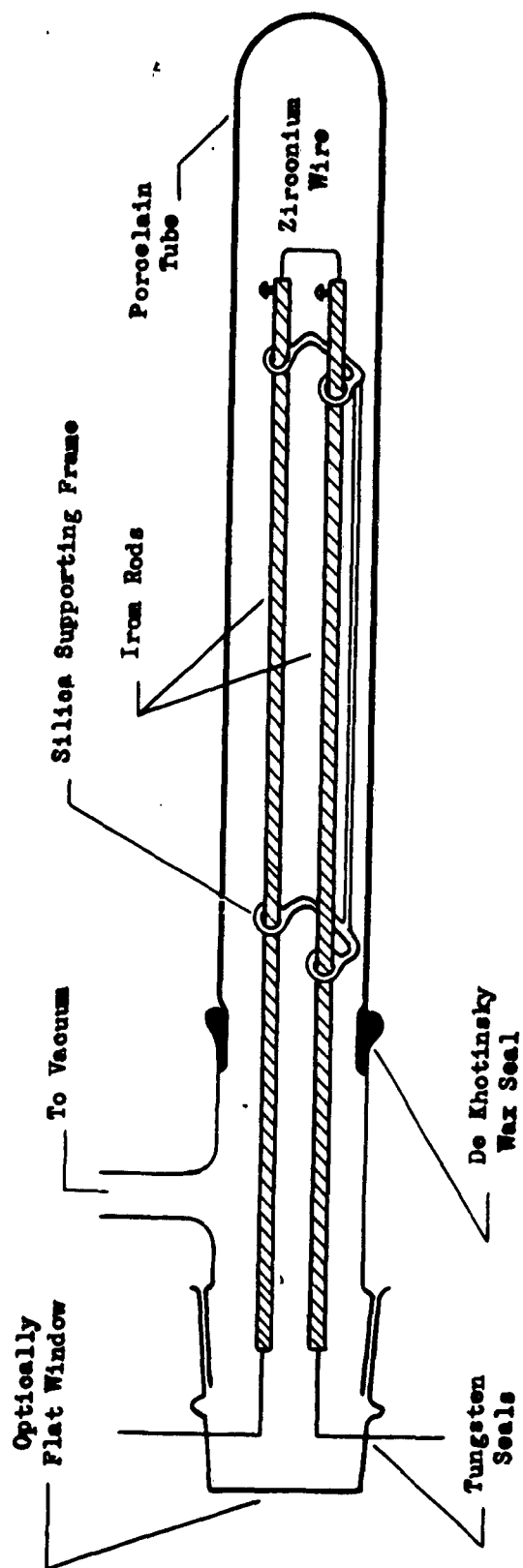


Fig. 1 Apparatus for Preparing Zirconium-Oxygen Alloys.  
 (Iron rods served as electrodes for conducting current through Zr wire)

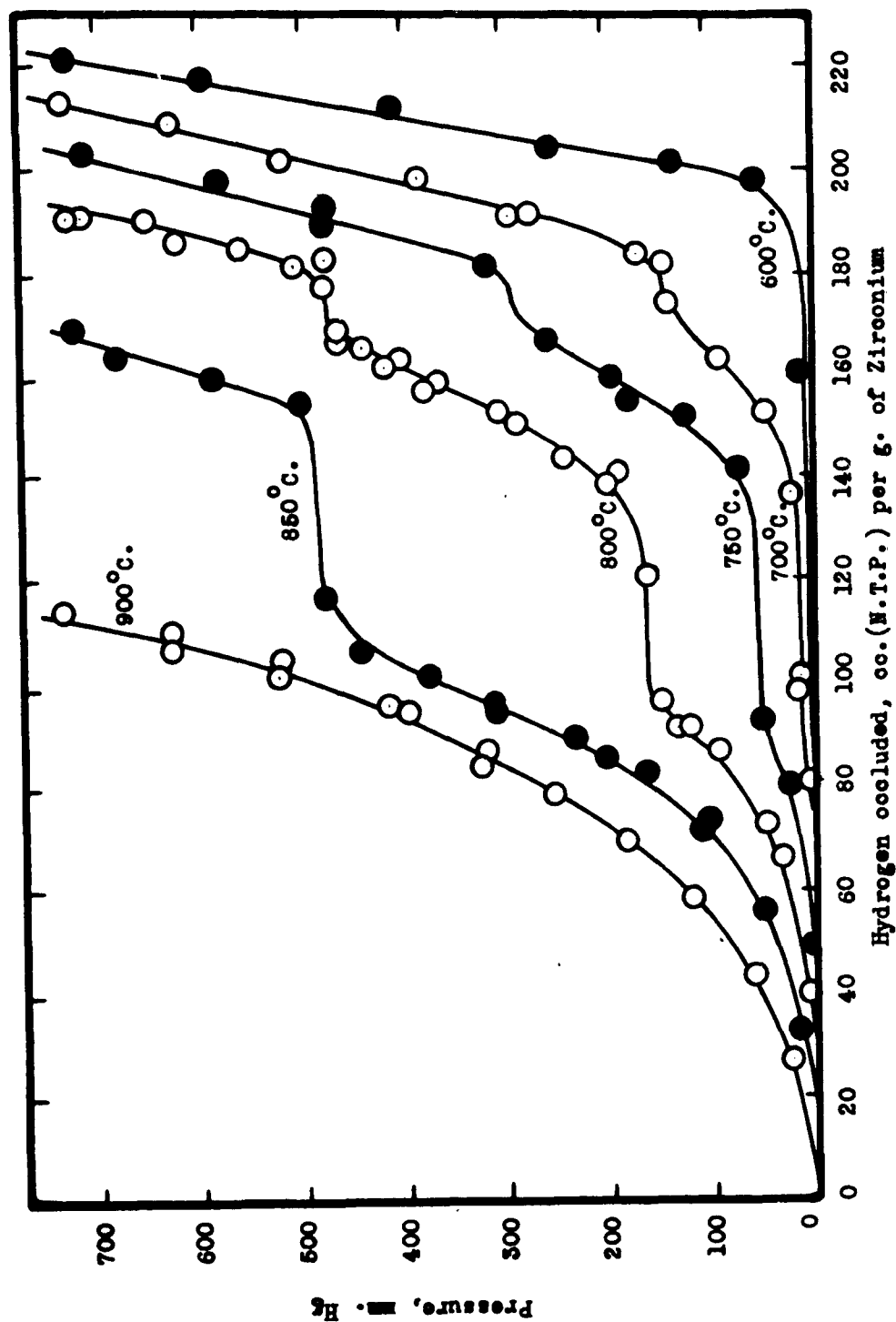


Fig. 2 Isothermal Pressure-Volume Curves for an Alloy Containing Initially 6.3 Atom Per Cent Oxygen in the Temperature Range 600 to 900°C.  
( $R = 0.068$ )

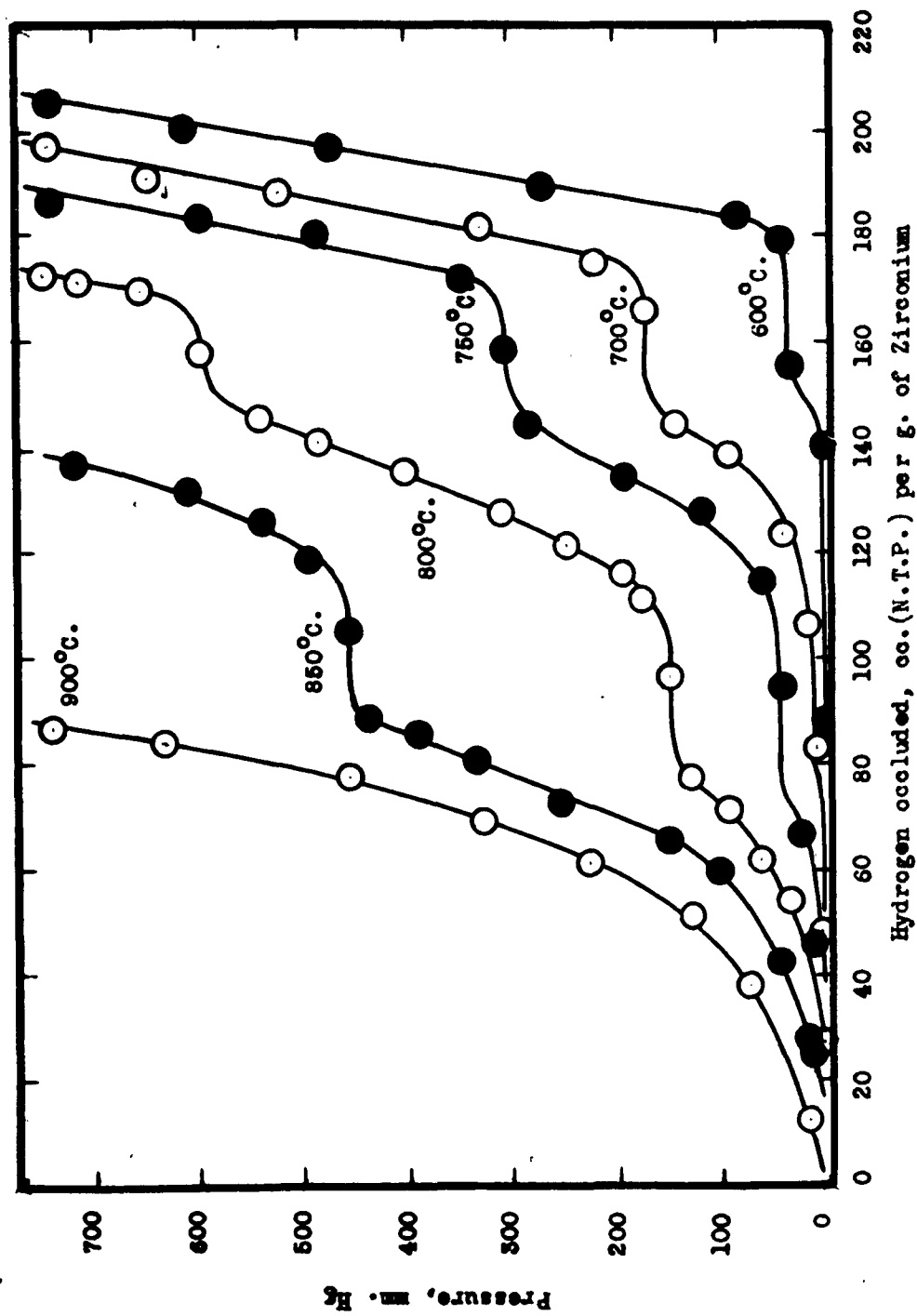


Fig. 3 Isothermal Pressure-Volume Curves for an Alloy Containing Initially 10.8 Atom Per Cent Oxygen in the Temperature Range 600 to 900°C. ( $R = 0.121$ )

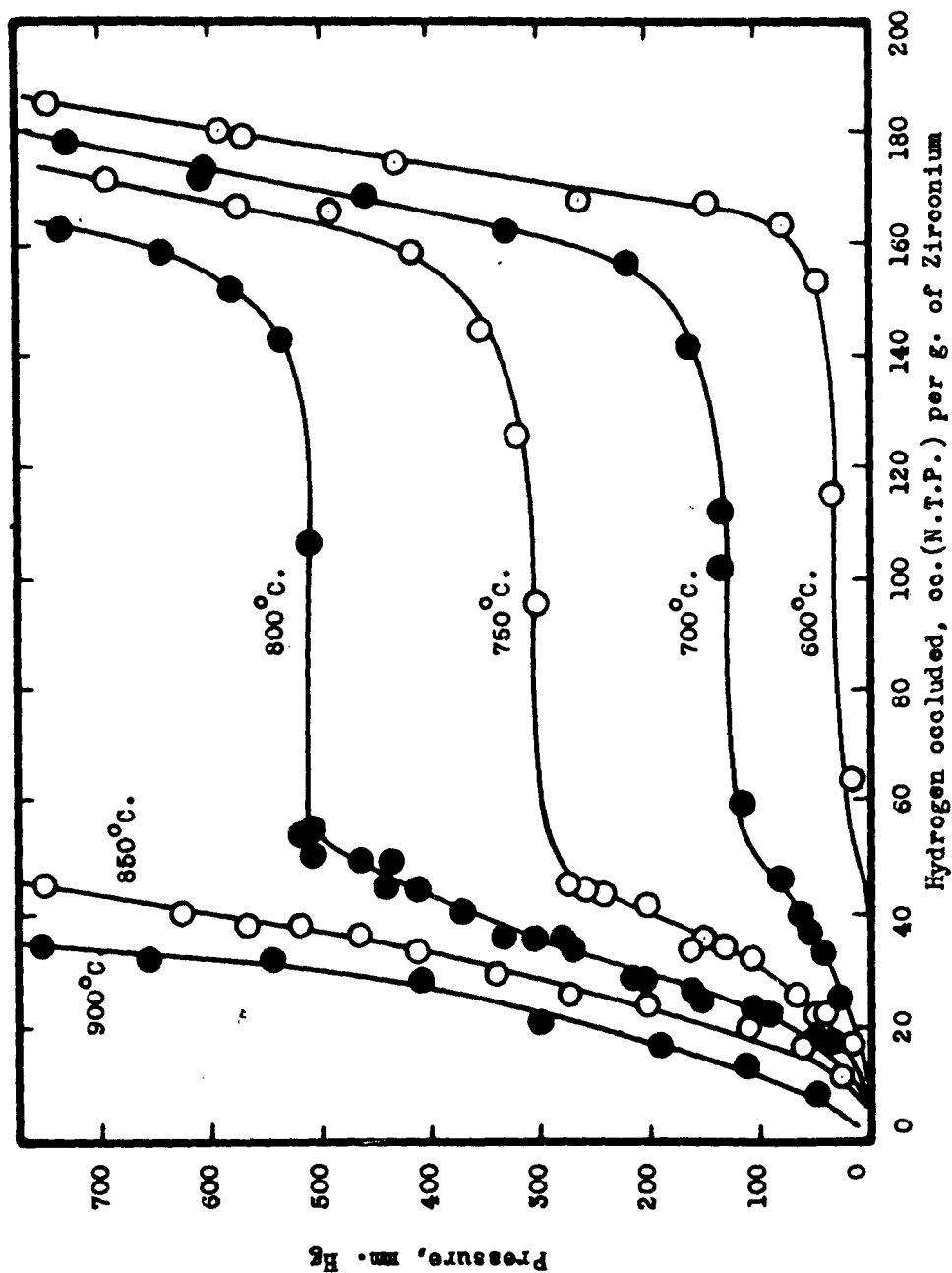


Fig. 4 Isothermal Pressure-Volume Curves for an Alloy Containing Initially 18.6 Atom Per Cent Oxygen in the Temperature Range 600 to 900°C. ( $R = 0.229$ )

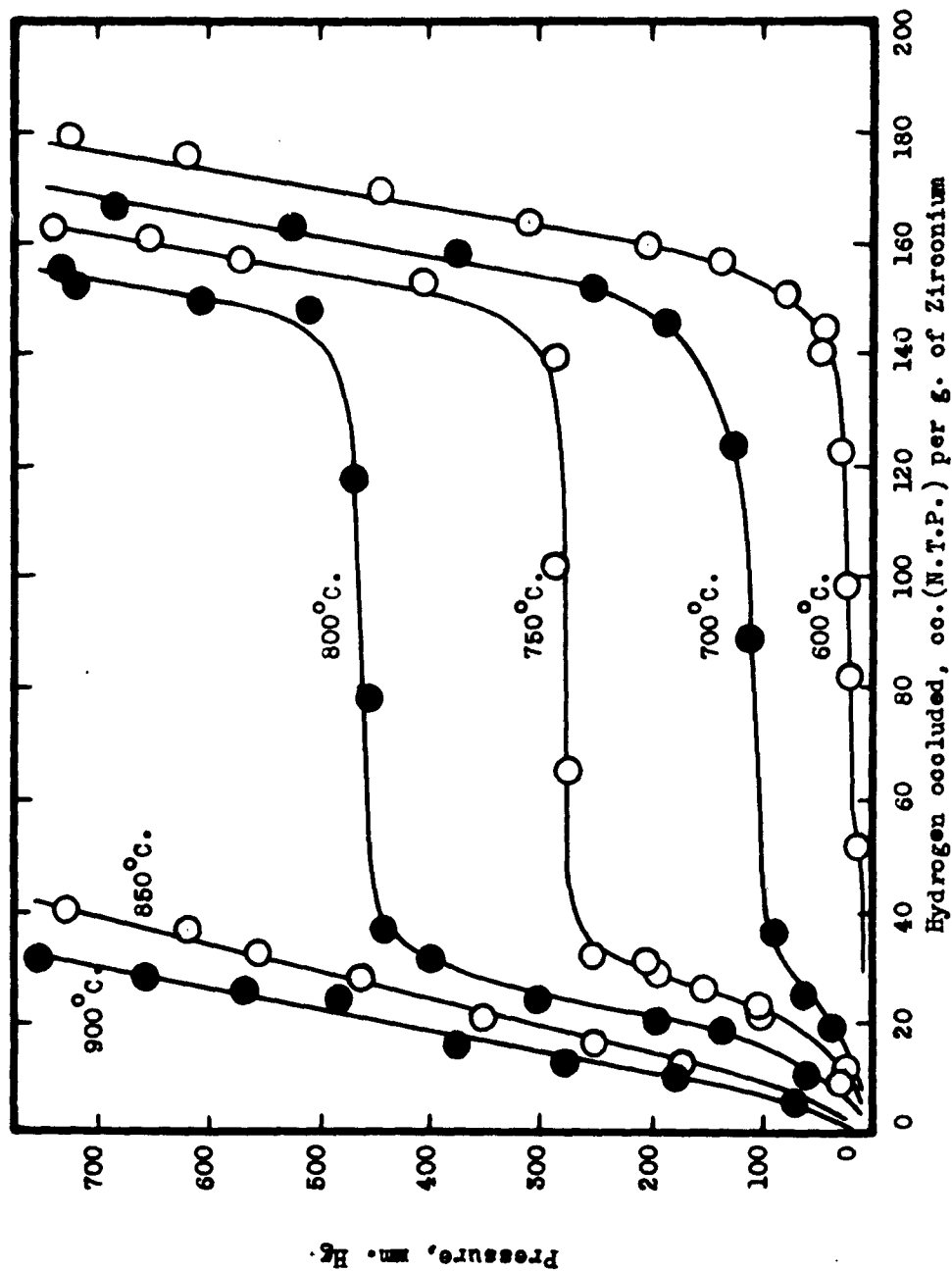


Fig. 5 Isothermal Pressure-Volume Curves for an Alloy Containing Initially 24.7 Atom Per Cent Oxygen in the Temperature Range 600 to 900°C. ( $R = 0.328$ )



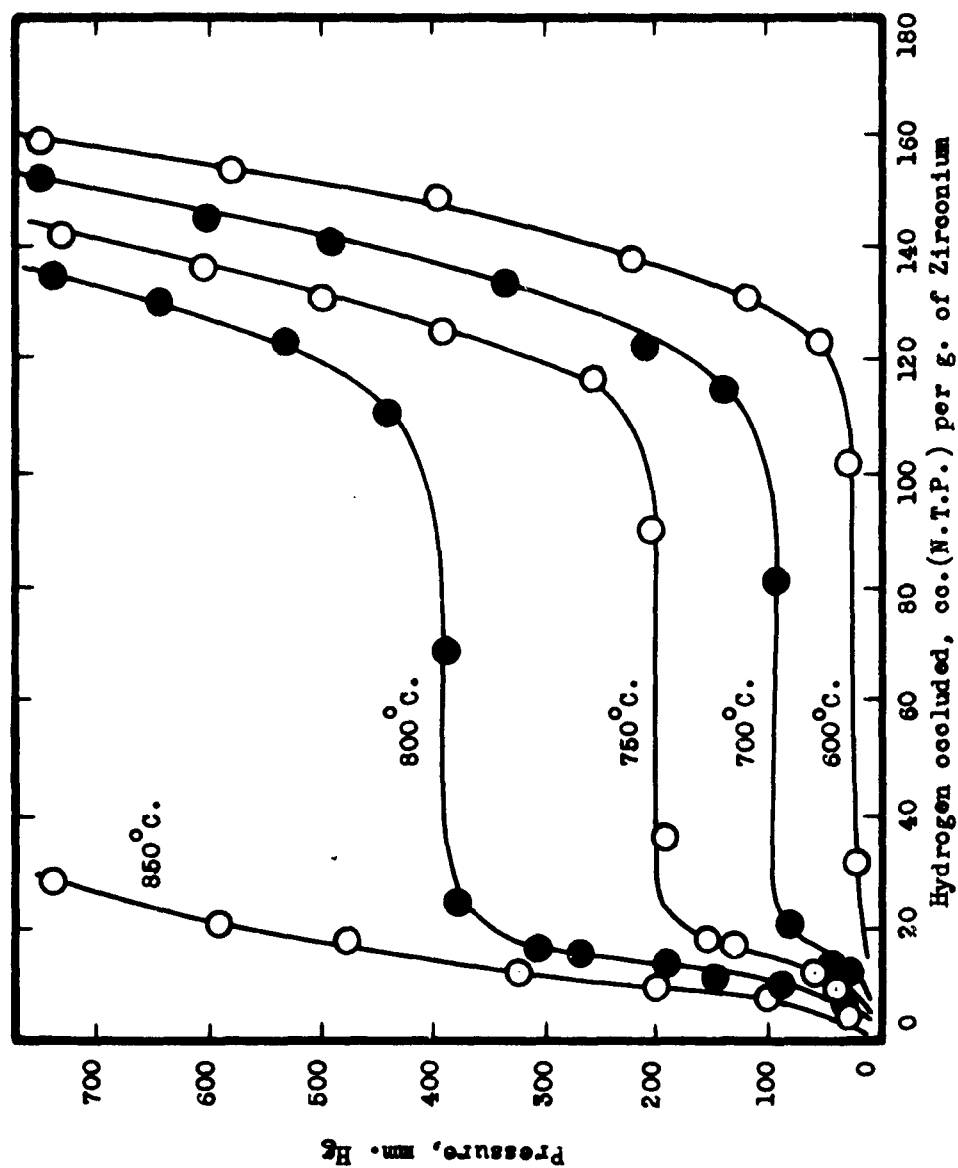


Fig. 6 Isothermal Pressure-Volume Curves for an Alloy Containing Initially 29.6 Atom Per Cent Oxygen in the Temperature Range 600 to 850°C. ( $R = 0.420$ )

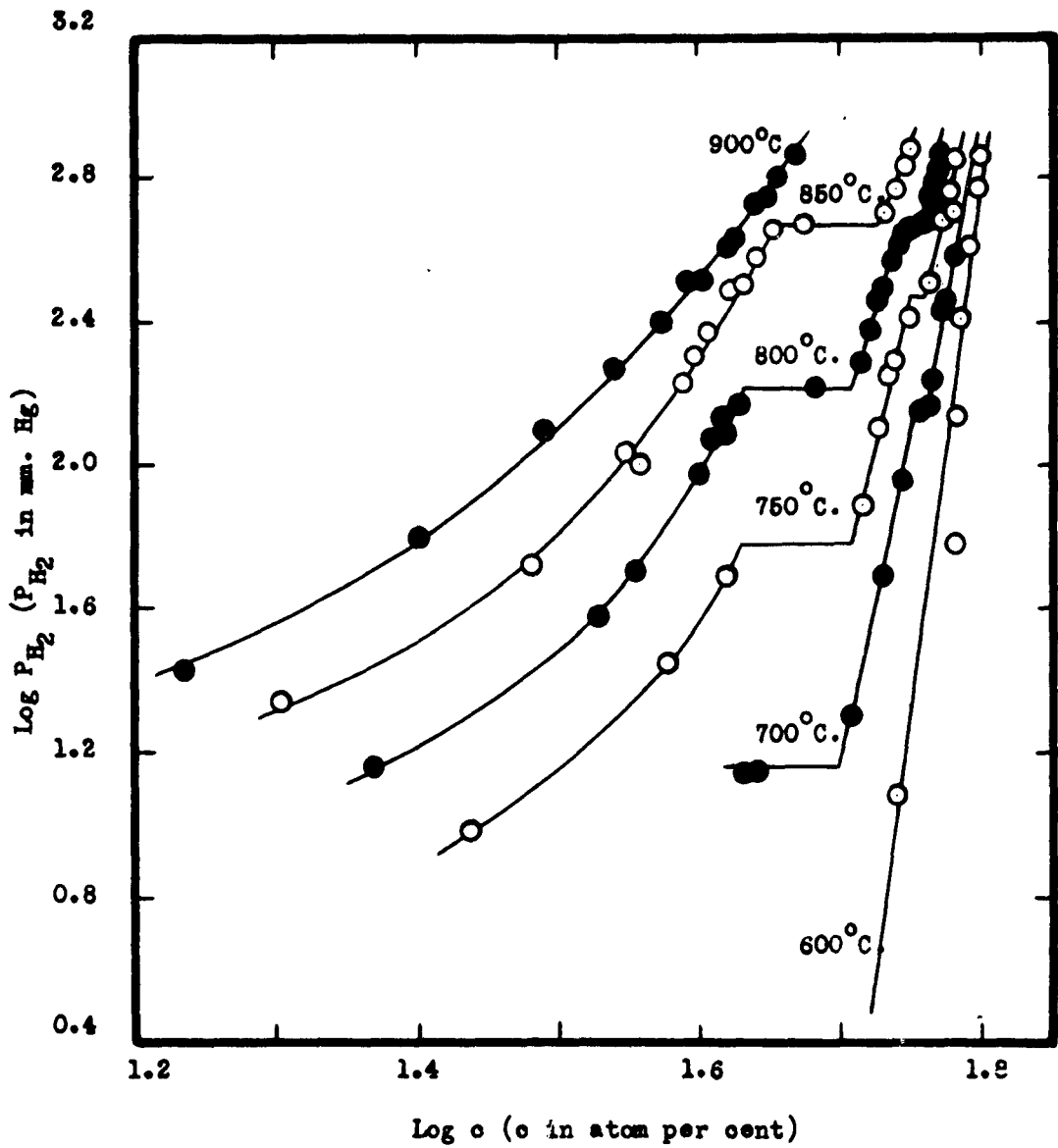


Fig. 7 Isothermal Pressure-Composition Logarithmic Plots for an Alloy Containing Initially 6.3 Atom Per Cent Oxygen. ( $R = 0.068$ )

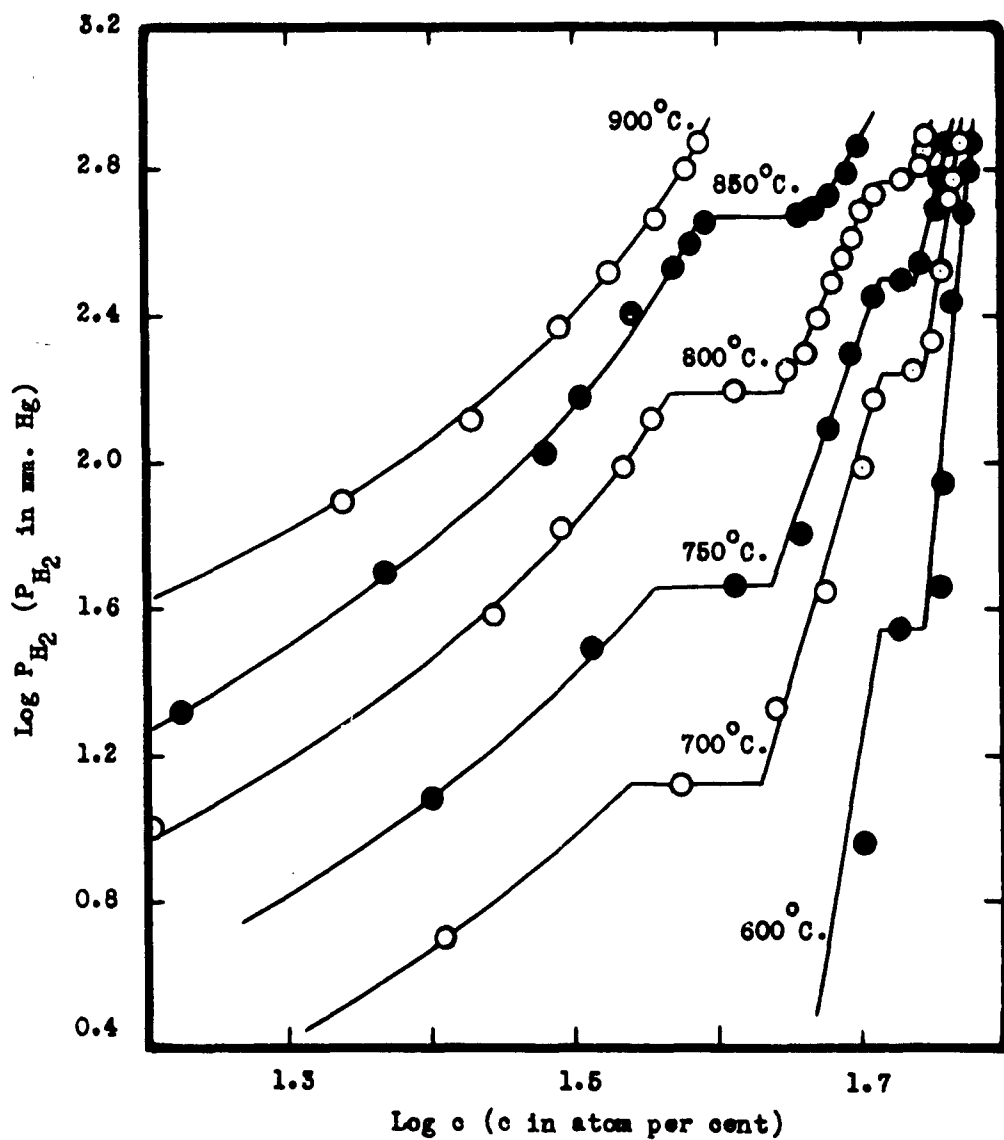


Fig. 8 Isothermal Pressure-Composition Logarithmic Plots for an Alloy Containing Initially 10.8 Atom Per Cent Oxygen. ( $R = 0.121$ )

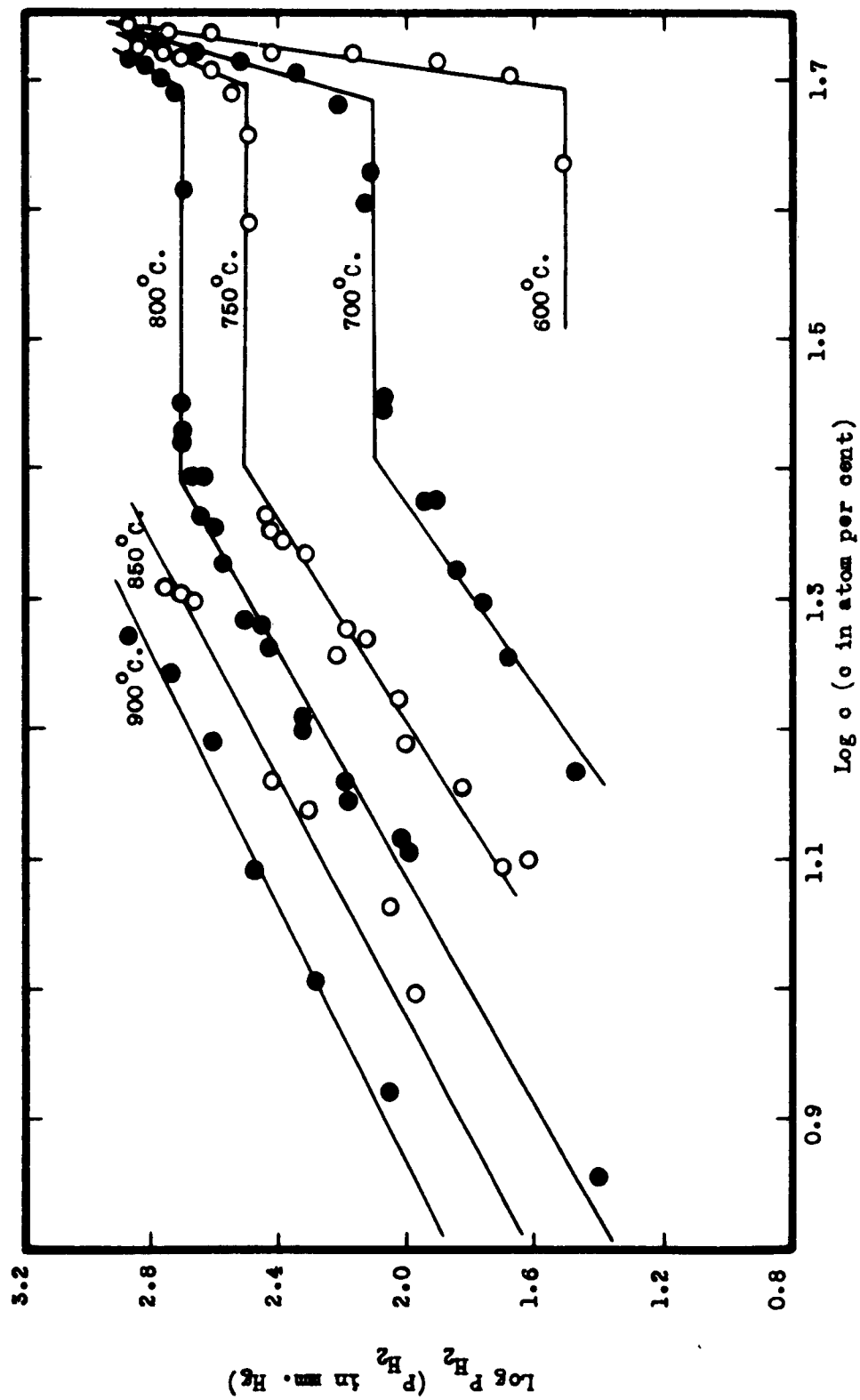


Fig. 9 Isothermal Pressure-Composition Logarithmic Plots for an Alloy  
Containing Initially 18.6 Atom Per Cent Oxygen.  
( $R = 0.229$ )

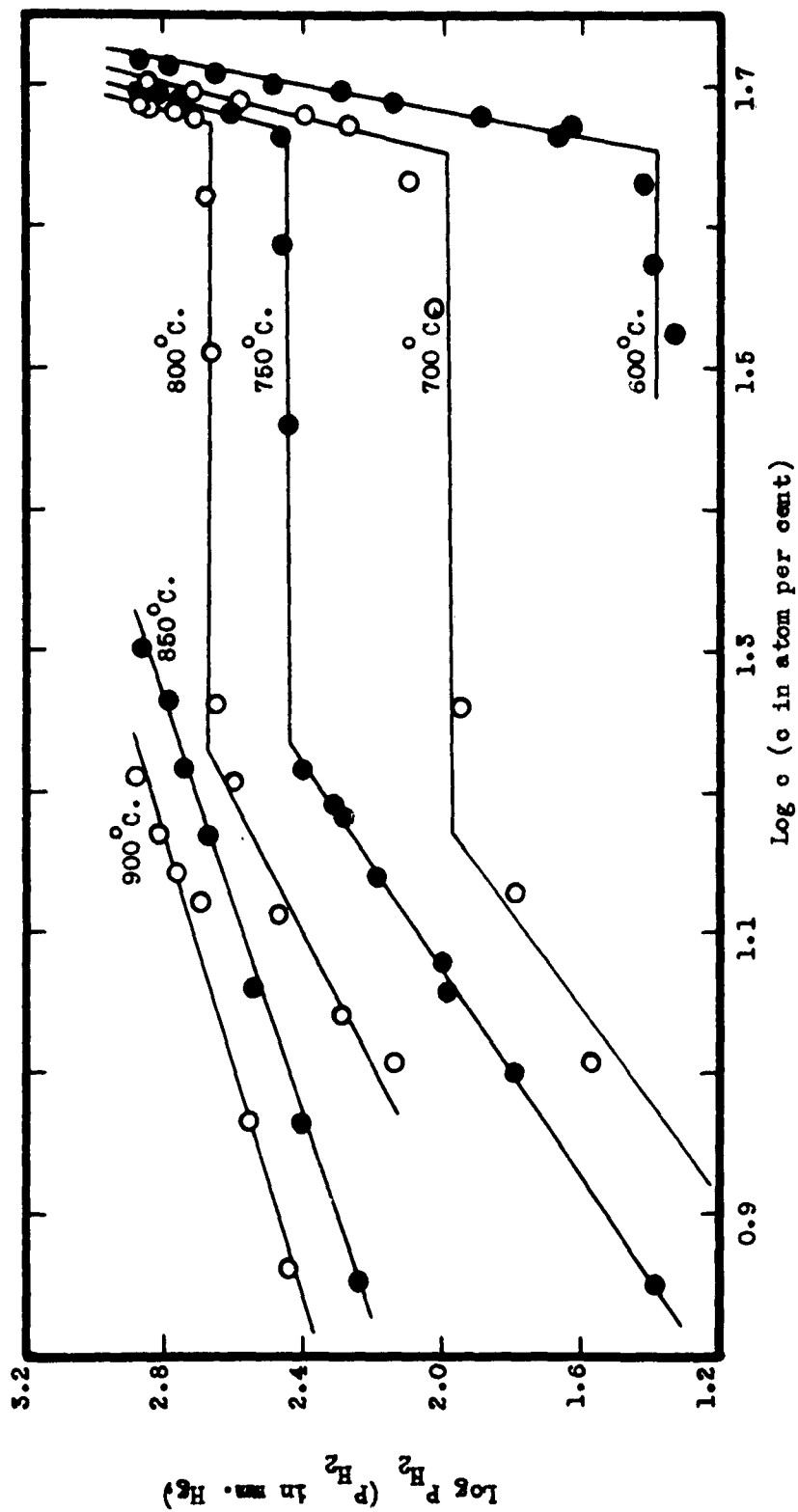


Fig. 10 Isothermal Pressure-Composition Logarithmic Plots for an Alloy  
Containing Initially 24.7 Atom Per Cent Oxygen.  
( $R = 0.328$ )

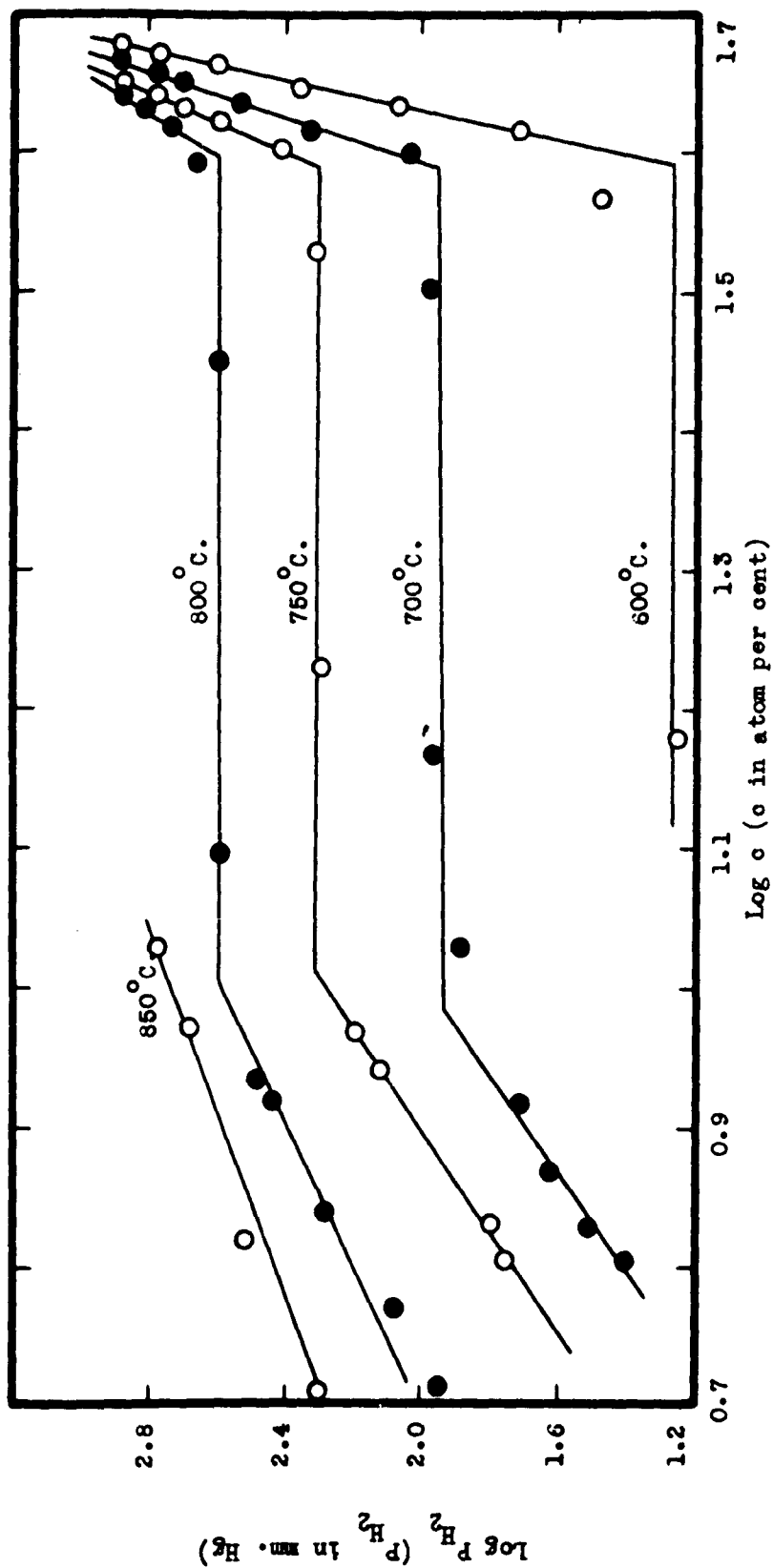


Fig. 11 Isothermal Pressure-Composition Logarithmic Plots for an Alloy Containing Initially 29.6 Atom Per Cent Oxygen.  
( $R = 0.420$ )

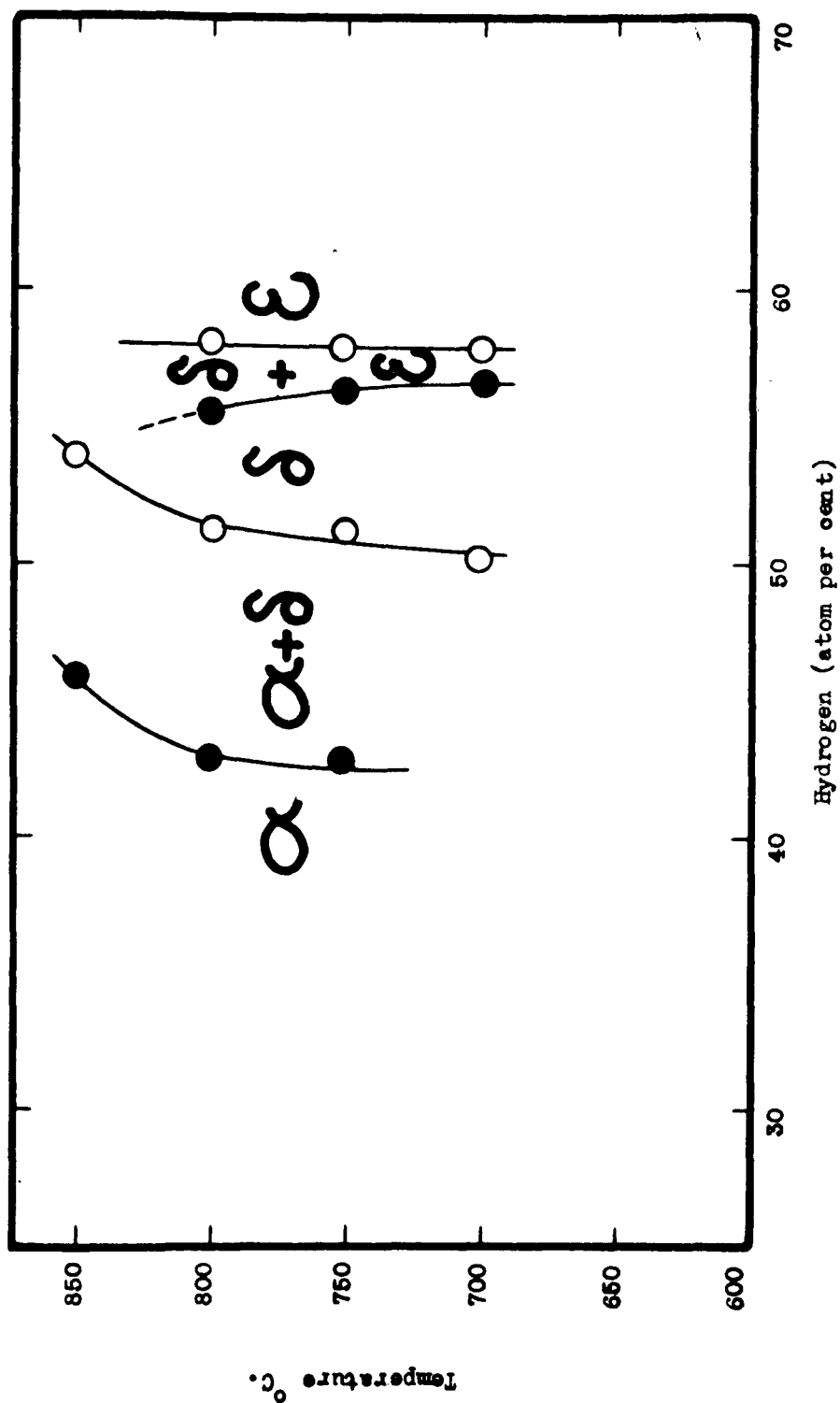


Fig. 12 Plot of the Boundary Compositions for the Two-Phase Fields in an Alloy Containing Initially 6.3 Atom Per Cent Oxygen.  
( $R = 0.068$ )

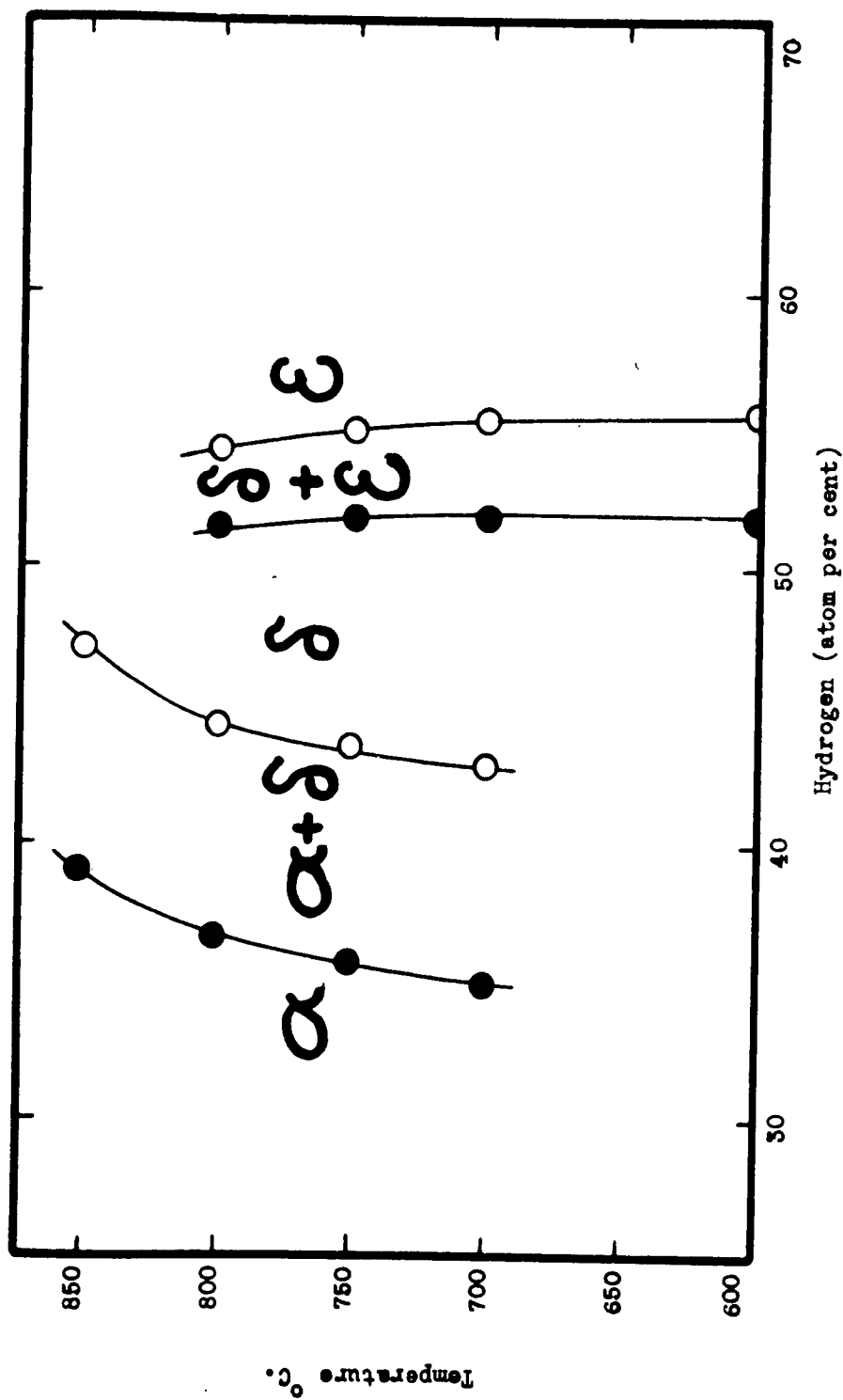


Fig. 13 Plot of the Boundary Compositions for the Two-Phase Fields in an Alloy Containing Initially 10.8 Atom Per Cent Oxygen. ( $R = 0.121$ )



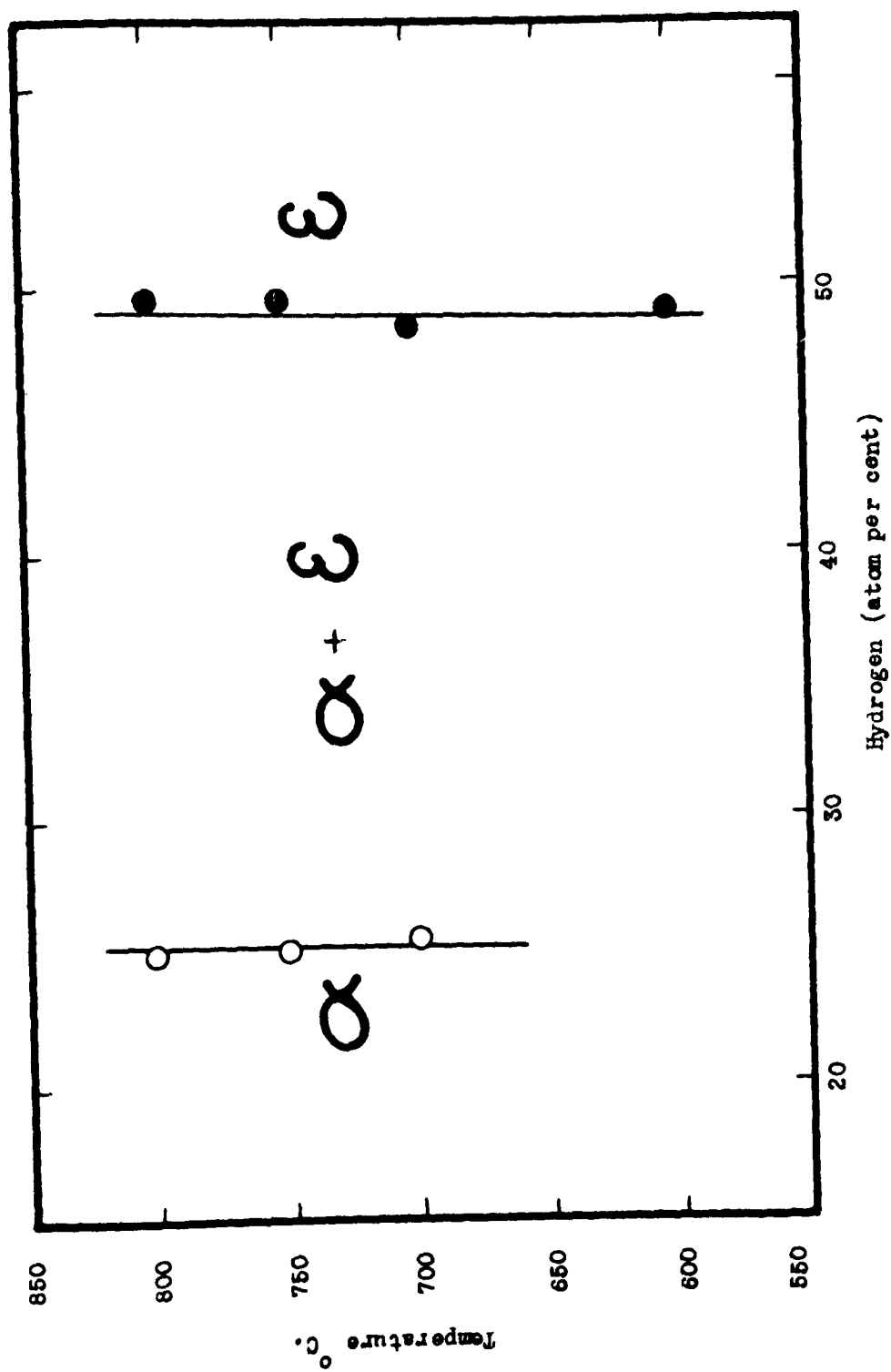


Fig. 14 Plot of the Boundary Compositions for the Two-Phase Field in an Alloy Containing Initially 18.6 Atom Per Cent Oxygen.  
( $R = 0.229$ )

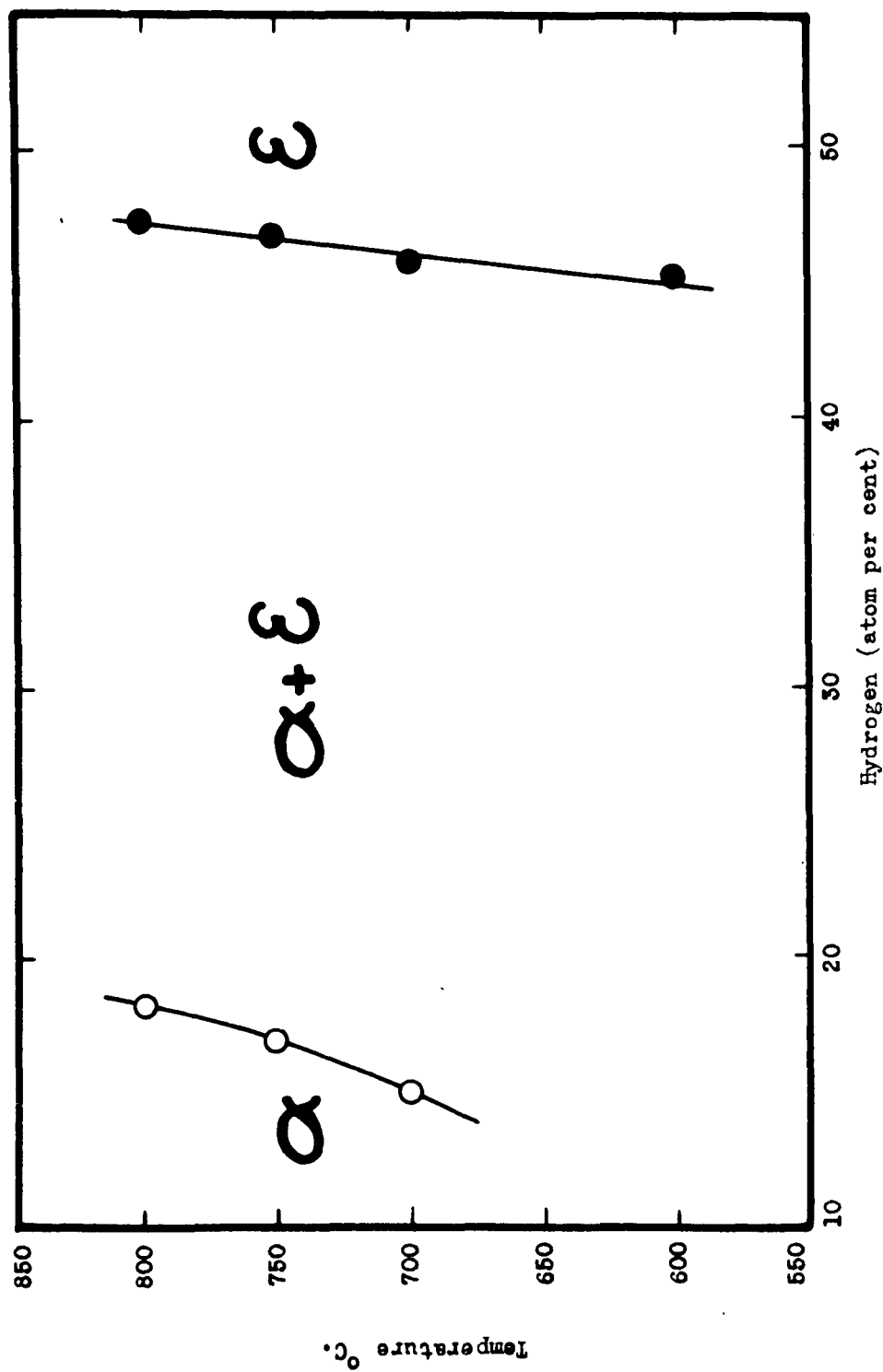


Fig. 15 Plot of the Boundary Compositions for the Two-Phase Field in an Alloy Containing Initially 24.7 Atom Per Cent Oxygen.  
( $R = 0.328$ )

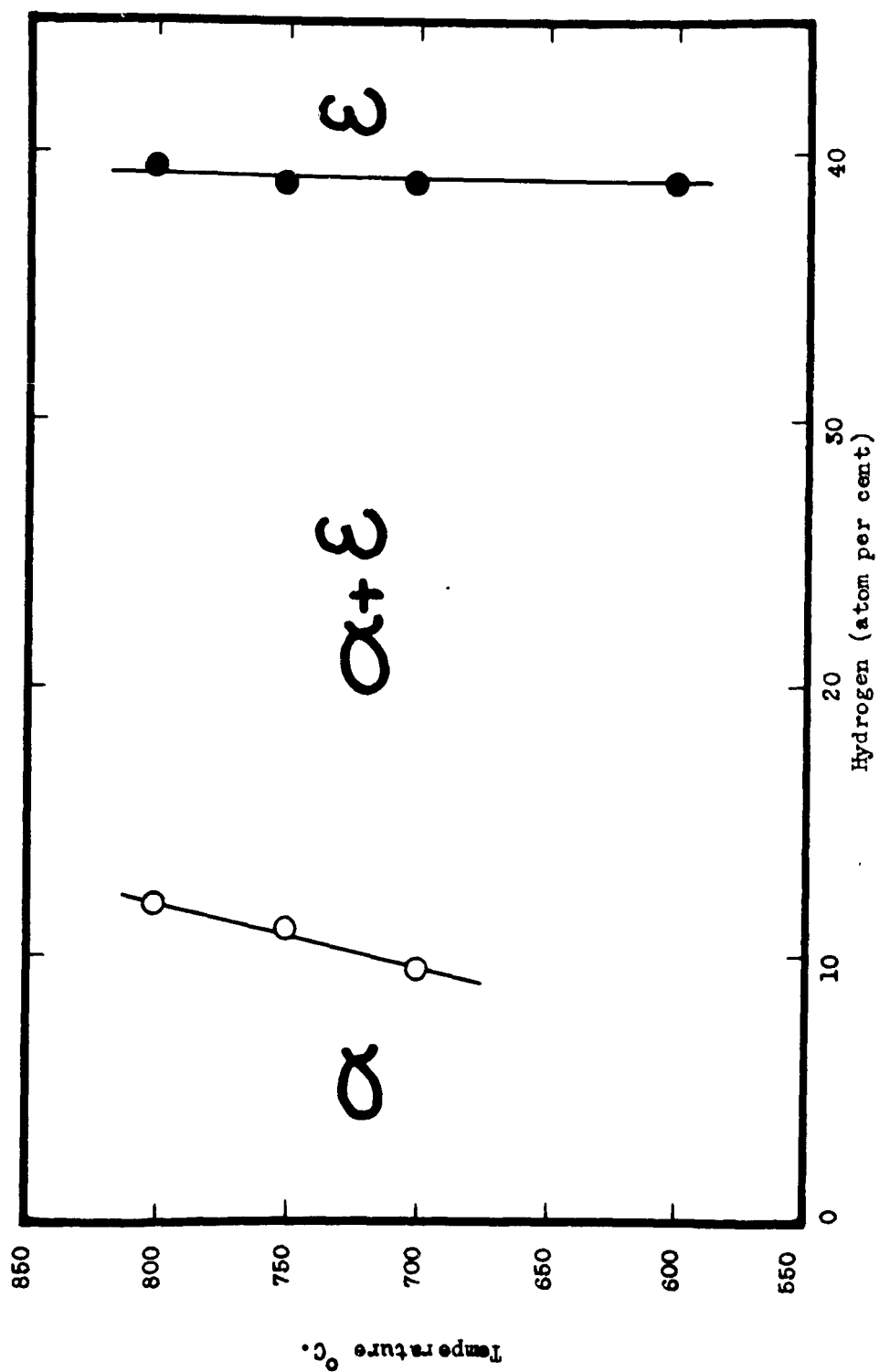


Fig. 16 Plot of the Boundary Compositions for the Two-Phase Field in an Alloy Containing Initially 29.6 Atom Per Cent Oxygen. ( $R = 0.420$ )

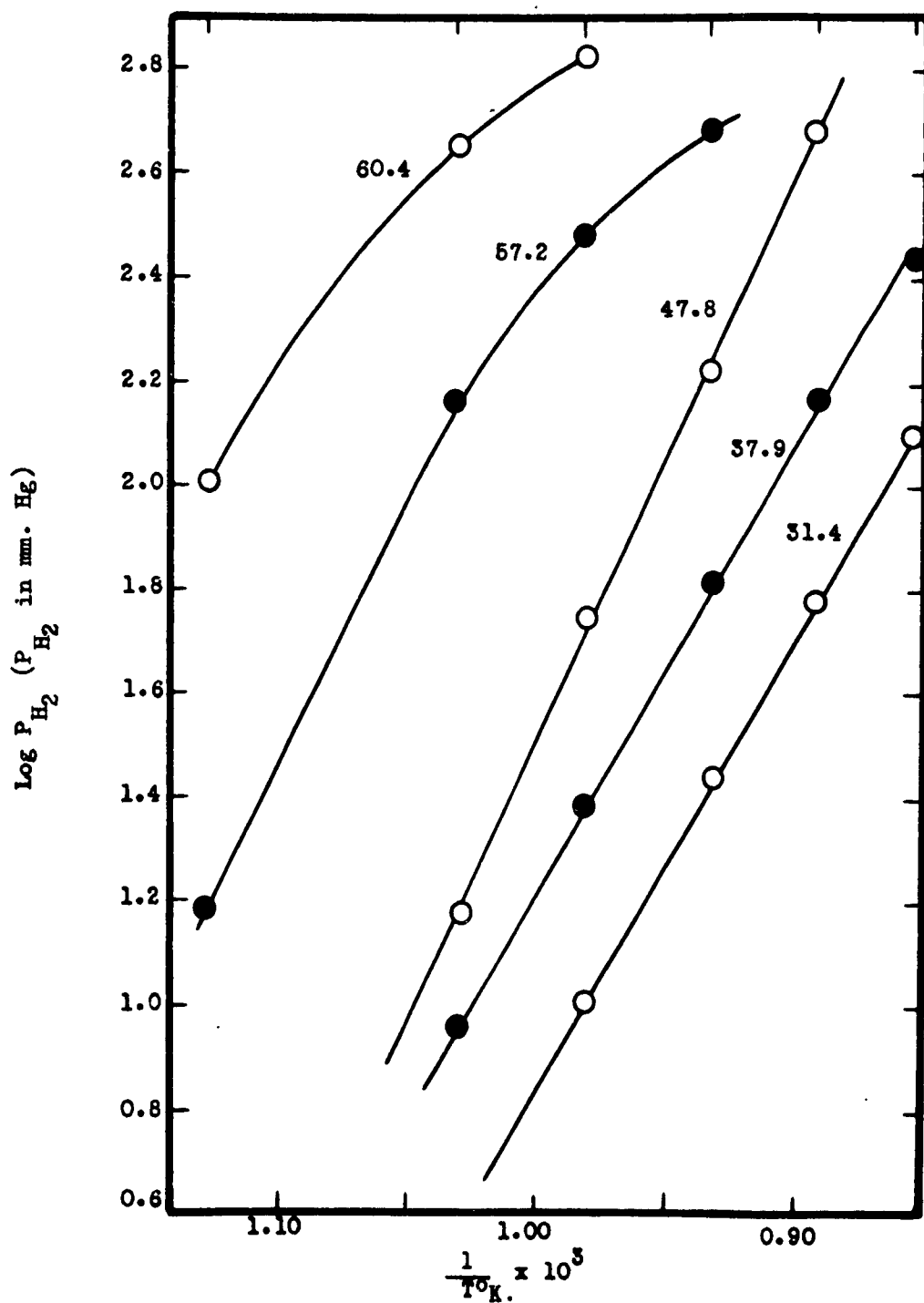


Fig. 17 Pressure-Temperature Curves for an Alloy Containing Initially 6.3 Atom Per Cent Oxygen in the Concentration Range 31.4 to 60.4 Atom Per Cent Hydrogen. ( $R = 0.068$ )

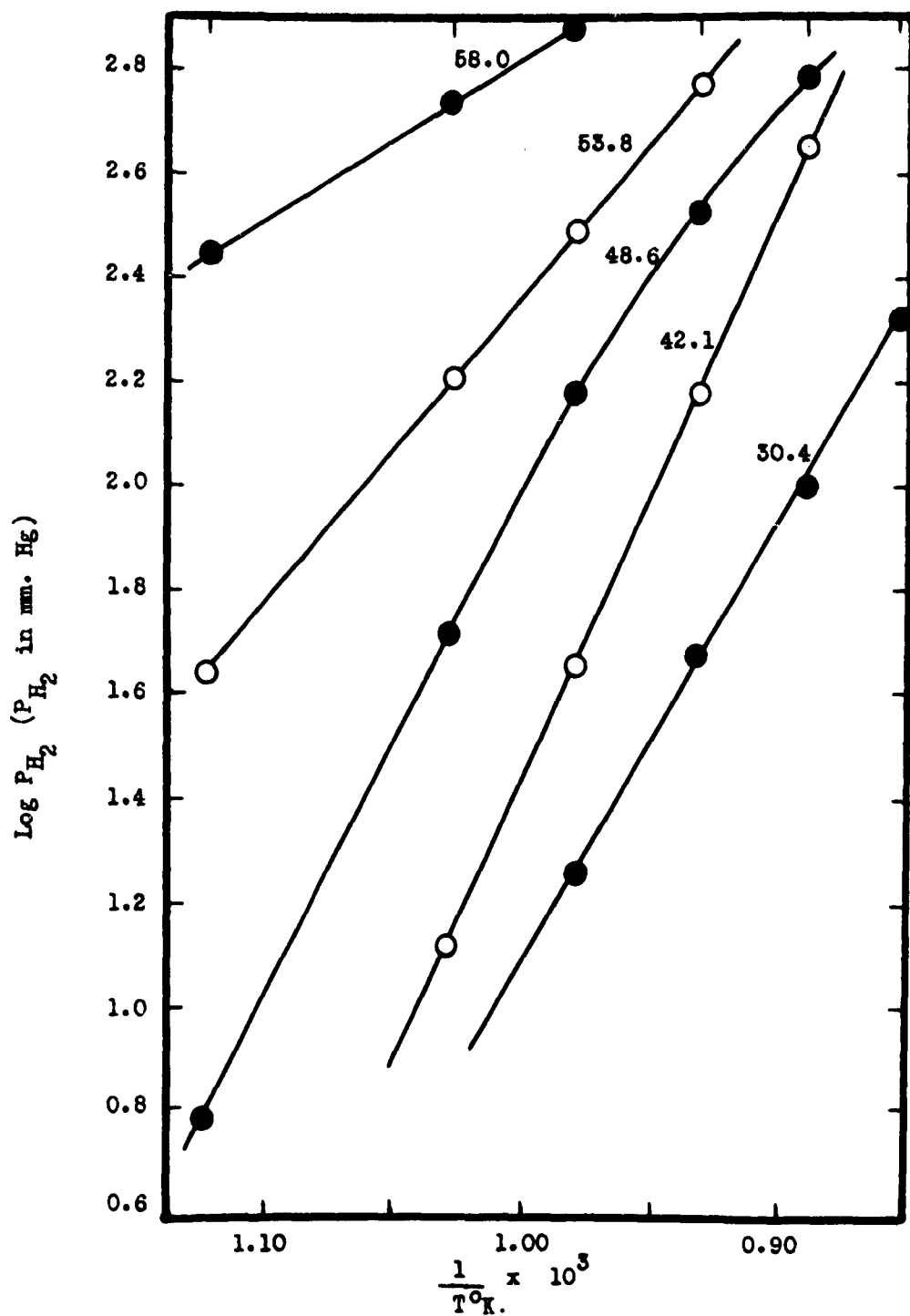


Fig. 18 Pressure-Temperature Curves for an Alloy Containing Initially 10.8 Atom Per Cent Oxygen in the Concentration Range 30.4 to 58.0 Atom Per Cent Hydrogen. ( $R = 0.121$ )

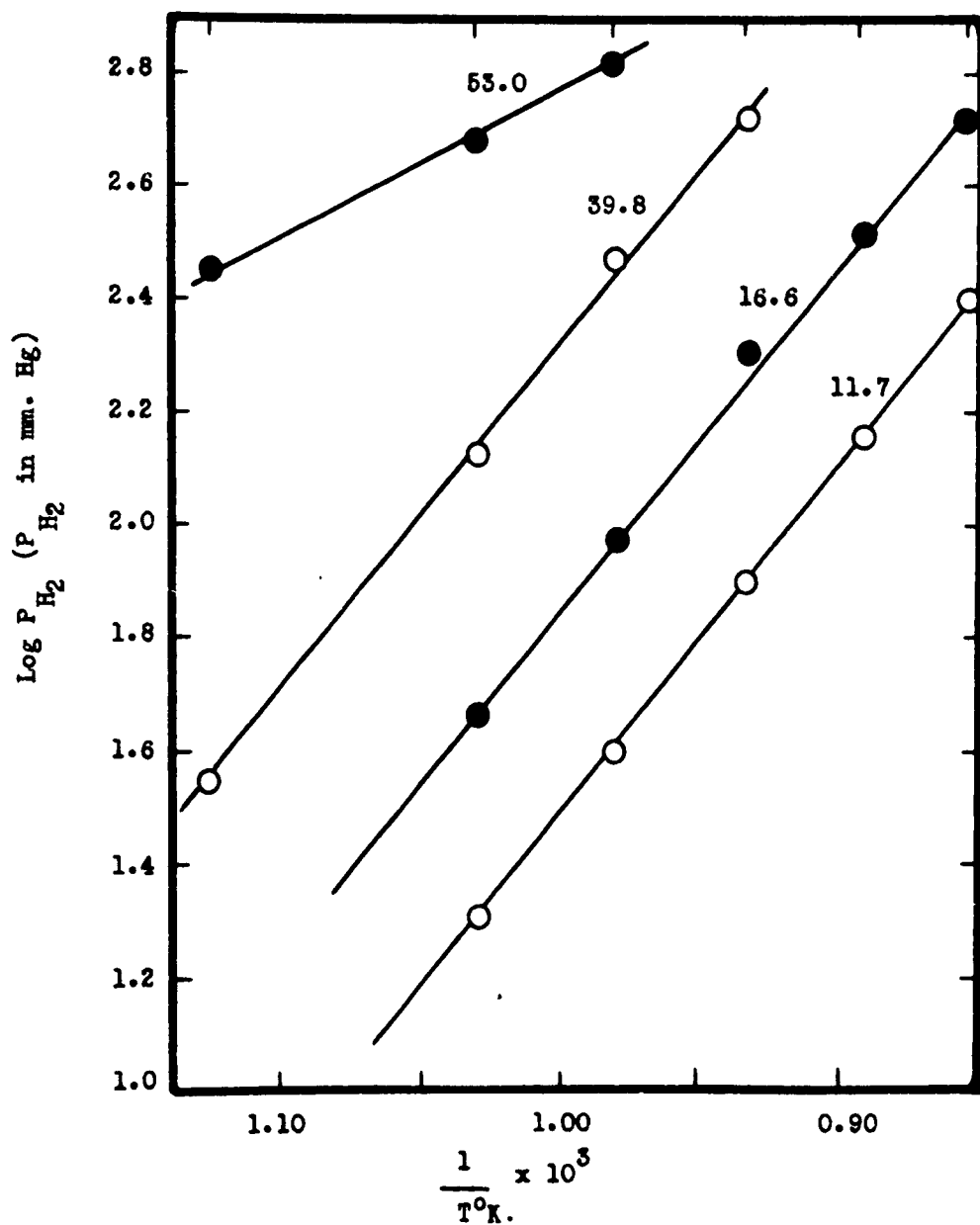


Fig. 19 Pressure-Temperature Curves for an Alloy Containing Initially 18.6 Atom Per Cent Oxygen in the Concentration Range 11.7 to 53.0 Atom Per Cent Hydrogen. ( $R = 0.229$ )

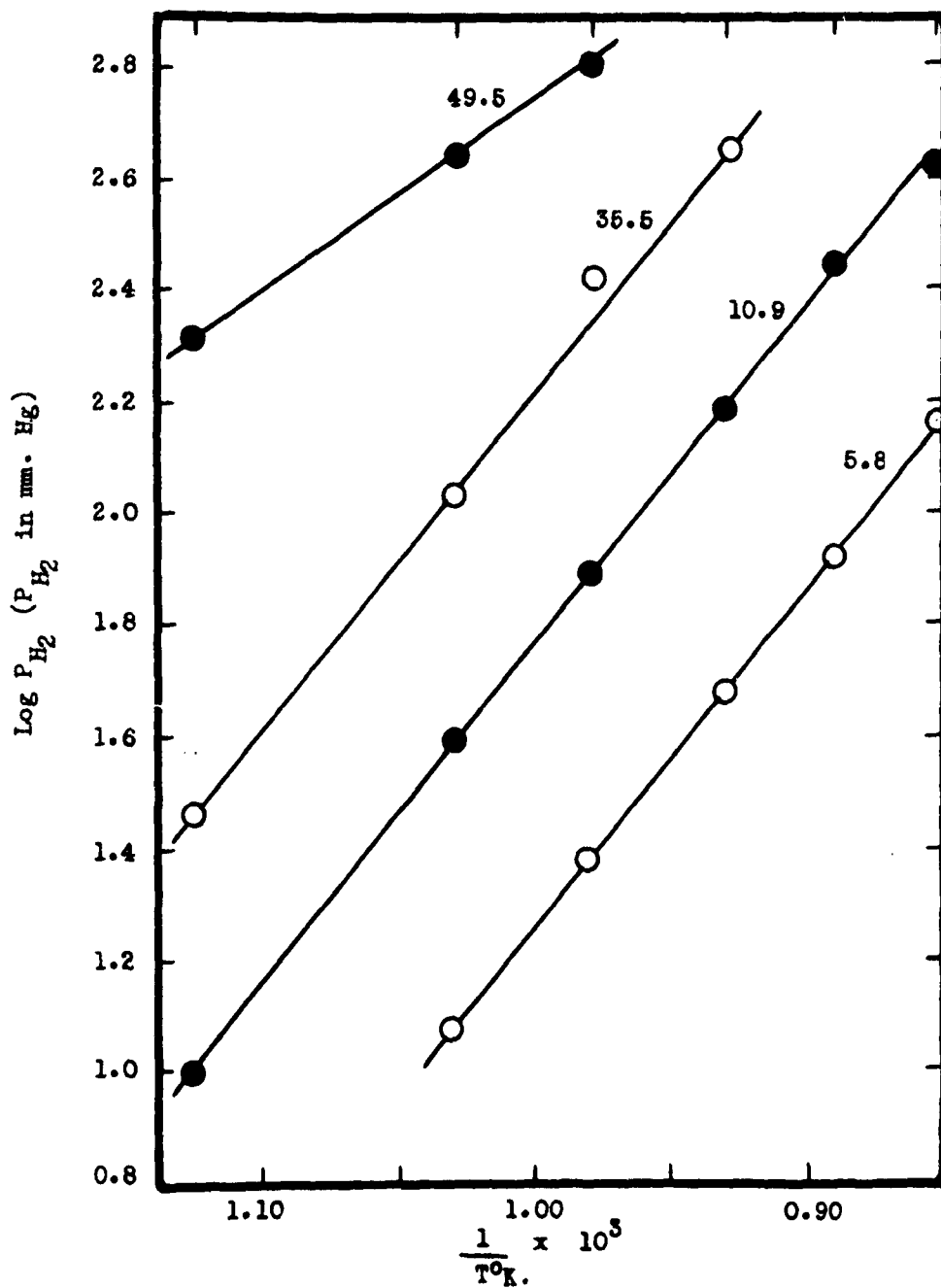


Fig. 20 Pressure-Temperature Curves for an Alloy Containing Initially 24.7 Atom Per Cent Oxygen in the Concentration Range 5.8 to 49.5 Atom Per Cent Hydrogen. ( $R = 0.328$ )

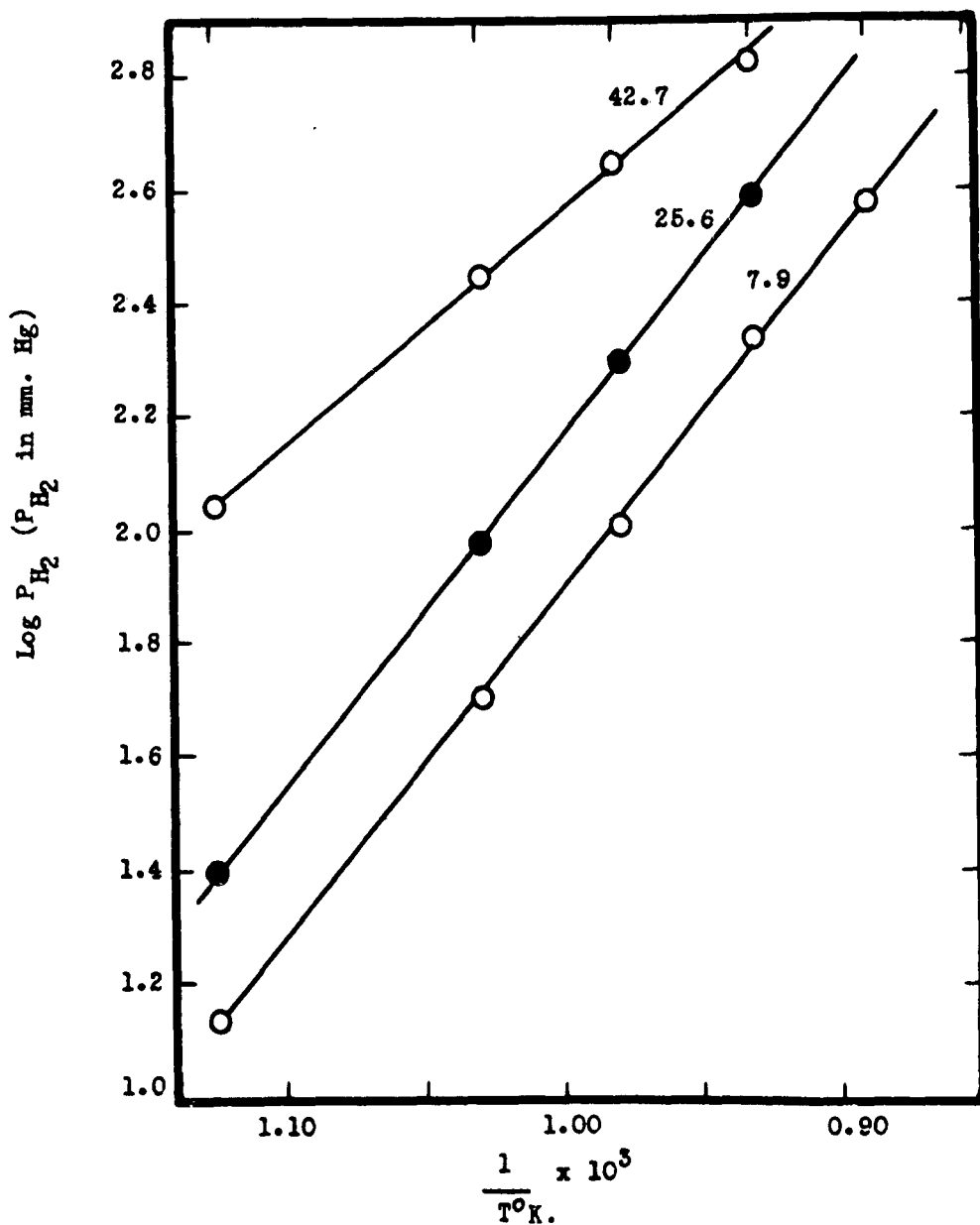


Fig. 21 Pressure-Temperature Curves for an Alloy Containing Initially 29.6 Atom Per Cent Oxygen in the Concentration Range 7.9 to 42.7 Atom Per Cent Hydrogen. ( $R = 0.420$ )



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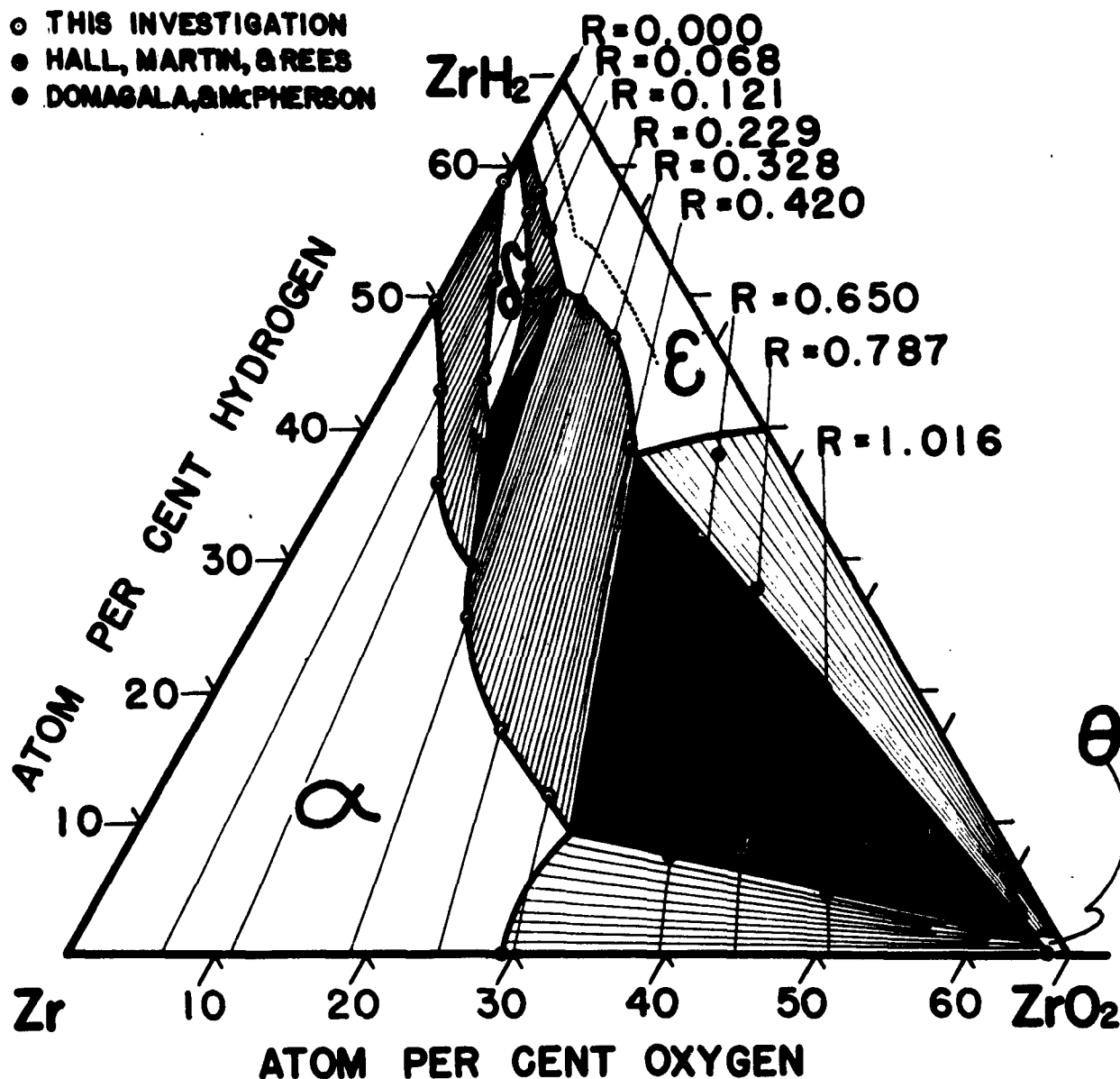


Fig. 22 Ternary System Zr-O-H

Provisional Phase Diagram in Part--Isothermal Cross Section at 750°C.

Two-phase regions are shaded by lines approximating tie-lines. Three-phase regions are drawn in solid black. Extensions of boundaries beyond experimental data is by inference and therefore must be considered provisional. The lines across the diagram leading to R values represent experimental composition traverses as hydrogen was successively added to Zr-O solid solution specimens of constant O/Zr atom ratios, R. Dotted line represents a contour of the variation in composition at constant hydrogen pressure of 760 mm.